SUMMARY OF THE THESIS

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THE THERMODYNAMIC ACTIVITY OF SILICON IN LIQUID IRON

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by

G. M. Smith, B. Sc.

April, 1963

At the commencement of the research work reported here, disagreement existed in the published literature between values of the thermodynamic activity of silica in slags determined by different workers. Activity values obtained through direct pressure measurements on reaction (1),

$$SiO_{2(slag)} + 3C_{(gr)} = SiC_{(s)} + 2CO_{(g)} \qquad (1)$$

differed in magnitude by 4 : 1 from the silica activities obtained through a distribution study of the silicon/silica ratio in reaction (2) at 1600°C for graphite saturated iron.

$$SiO_{2(slag)} + 2C = Si_{(in\ Fe)} + 2CO_{(1Atm)} \qquad (2)$$

Activity values derived from the data on reaction (2) depend upon a reliable knowledge of the activity of silicon in carbon saturated iron. Values of the activity of silicon in both binary and ternary iron silicon and iron carbon silicon solutions had been previously obtained from a study of the distribution of silicon between immiscible liquid silver and iron solutions. In view of the disagreement on the silica activities and because of certain discrepancies in the conversion of the latter silicon distribution ratios to their corresponding silicon activity values in the iron solutions, the present research work was undertaken.

The distribution of silicon between liquid iron and silver has been redetermined at 1570°C, and extended to lower mole fractions of silicon in iron than had been hitherto obtained. To make this work possible an accurate method for the chemical analysis of silicon in silver at very low concentrations was required. No method could be found in the literature, hence a large part of the present work consisted of developing a reliable technique for this analysis. Two methods were found both involving the photometric measurement of silicon as the yellow-green silicomolybdate complex in acid solution, and each provided a useful check on the other.

The extension of the distribution measurements in the binary solutions to lower concentrations of silicon enabled data in the ternary iron carbon silicon solutions to be extended to higher carbon concentrations. Distribution measurements on the ternary system were therefore made at 1500°C with high carbon concentrations. When adjustment is made for temperature, the present experimental data agree well with the results of the earlier workers.

Calculation of silicon activities in iron solutions from the distribution data requires a knowledge of the activity of silicon in silver solutions about which there was some uncertainty. A reliable value for the latter was obtained

from a study of the solubility in silver solution in equilibrium with silicon carbide at 1450°C and 1500°C. Reaction (3) governs this equilibrium.

$$Si_{(L)} + C_{(gr)} = SiC_{(s)} \qquad (3)$$

The activity coefficient of silicon in silver solutions was calculated from the solubility data of the present work and from the published data on the free energy change accompanying reaction (3). Silicon in silver solutions has been shown to obey Henry's Law at the low concentrations of this study, and this permits the presently derived activity coefficient to be used in calculating silicon activities in the iron solutions from the distribution data. Since carbon is insoluble in liquid silver the same procedure was used to obtain values of the activity of silicon in the ternary solutions at 1500°C.

The recently revised value of the free energy of formation of silica has been used along with the published thermodynamic data on carbon monoxide and for reaction (1) to establish the free energy equation for reaction (3).

Publsihed data on iron carbon silicon solutions in equilibrium with silicon carbide have been employed in calculating silicon activities in the binary solutions and these are shown to be in good agreement with those derived from the present results.

The revised value for the free energy of silicon has been used to recalculate the equilibrium constant in reaction (2) and this has been employed along with the present silicon activity values to recalculate silica activities from the previous data on reaction (2).

The silica activities derived from the data on this reaction are now shown to be in good agreement with those obtained from the data on reaction (1).

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C O N T E N T S

INTRODUCTION

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The measurement of the thermodynamic activities of components dissolved in liquid iron and slags at iron and steel-making temperatures leads to a better understanding of, and more control over, the reactions which occur in the manufacture of iron and steel. Unfortunately, errors of measurement can appear in the published literature, and because of the interrelated nature of thermodynamic data can give rise to major discrepancies amongst the results of different investigators purporting to measure the same thermodynamic quantities.

At the commencement of this research, values of the activity of silica in lime-silica and lime-alumina-silica slags calculated from the experimental data of various investigators showed serious disagreement well outwith the range of experimental error. In particular, the results of Baird and Taylor[1], later confirmed and extended by Kay and Taylor[2], and those of Langenberg and Chipman[3] who continued and extended earlier work of Fulton and Chipman[4], differed by approximately 4 : 1 in magnitude, although their activity composition curves showed excellent agreement in shape. Both sets of data were consistent within themselves but the results of Kay and Taylor[2] at the lower end of their high a_{SiO_2} range overlapped sufficiently with those of Langenberg

and Chipman[3], who worked at low a_{SiO_2} values, to show the large difference between the two sets of data. Senbongi and Omori[8] also calculated silica activities by determining the reversible E.M.F. values in a double cell and, allowing for temperature, their data agreed well with the results of Kay and Taylor[2].

These latter workers measured silica activities in lime-alumina-silica slags at 1450°C, 1500°C and 1550°C through the equilibrium pressure for the reaction:-

$$SiO_2 + 3C = SiC + 2CO \quad \ldots\ldots\ldots\ldots\ldots(1)$$

The value for the free energy of formation of silicon carbide was also calculated for the reaction (1) with pure silica. This was derived from the free energy change obtained for the above reaction combined with the values for carbon monoxide[6] and the accepted value for silica[6] (quartz). Heat capacity data[7] for silicon carbide taken with the above free energy value was then used to calculate $H^{\circ}(298{\cdot}16^{\circ}K) = -8{,}700$ cals.

The heat of formation of silicon carbide from crystalline silicon and graphite was reported by Humphrey, Todd, Coughlin and King[8] to be - 13,400 ± 920 cals/mole. This value was less negative than the value obtained by Drowart, De Maria and Inghram[9], using a mass spectroscope technique, by approximately 5 K.cals. Chipman[10] suggested that in the work of Baird and Taylor[1] on reaction (1), during the high temperature evacuation of their reaction tube, some silicon was produced according to the reaction:-

$$SiO_2(s) + 2C_{(gr)} = Si_{(l)} + 2CO$$

which condensed in the inside of the tube, so that the measured pressures were not true equilibrium pressures for reaction (1). Kay and Taylor[2] eliminated this possibility by a modified experimental arrangement, and confirmed Baird and Taylor's original results.

Fulton and Chipman[4] and later Langenberg and Chipman[3] obtained values for the activity of silica in lime-alumina-silica slags from studies of the equilibrium concentrations of silicon and silica in liquid iron and slag through the reaction:-

$$SiO_2(\text{in slag}) + 2C_{(gr)} = \underline{Si}^{+}(\text{in Fe}) + 2CO(1\ \text{atm})\ \text{at}\ 1600°C \quad \ldots\ldots(2)$$

Their method consisted of bringing carbon saturated liquid iron into equilibrium with the slag, held at temperature under carbon monoxide gas at one atmosphere pressure.

Under these conditions, $a_{Si}/a_{SiO_2} = K_2$

where K_2 represents the equilibrium constant for reaction (2). They then used the accepted values for the free energies of formation of silica and carbon monoxide and the activity coefficient of silicon in carbon saturated, liquid iron solution, to calculate a_{SiO_2} in the slags through K_2. Silica activities in slags

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+ $\underline{Si}$ is used to denote solution of silicon in liquid iron. Same notation will also be used for other solutes.

derived in this manner thus depend upon a reliable knowledge of the activity coefficient of silicon dissolved in liquid iron and iron-carbon solutions.

Chipman, Fulton, Gokcen and Caskey[11] obtained values for the activity coefficient of silicon in these solutions from the results of their study of the distribution of silicon between the two immiscible solvents, liquid iron and silver, at 1420°C.

At equilibrium, the chemical potential or activity of the silicon dissolved in each of these two immiscible liquids is the same. Hence at any given temperature,

$$\log N_{Si}^{Fe} \cdot \gamma_{Si}^{Fe} = \log N_{Si}^{Ag} \cdot \gamma_{Si}^{Ag} \text{ and so } \log N_{Si}^{Ag}/N_{Si}^{Fe} = \log \gamma_{Si}^{Fe} - \log \gamma_{Si}^{Ag} \quad \ldots\ldots\ldots\ldots(3)$$

Values of N_{Si}^{Fe} and N_{Si}^{Ag} are obtained by the chemical analyses of samples taken from each of the two phases.

At the very low concentrations of silicon in silver resulting from the distribution study, it is reasonable to assume that Henry's Law is valid, and there is experimental evidence to support this[12]. It follows therefore that in these experiments the activity coefficient of silicon in the silver layer is constant.

A plot of $\log N_{Si}^{Ag}/N_{Si}^{Fe}$ against N_{Si}^{Fe} will furnish the shape of the curve of $\log \gamma_{Si}^{Fe}$ against N_{Si}^{Fe} but to convert the

the scale of log N_{Si}^{Ag}/N_{Si}^{Fe} to the corresponding log γ_{Si}^{Fe} scale, either the value of log γ_{Si}^{Ag} or of log γ_{Si}^{Fe} at some particular value of N_{Si}^{Fe} must be determined.

Chipman et al[11] calculated values of γ_{Si}^{Ag}, and γ_{Si}^{Fe} at $N_{Si}^{Fe} = 0.73$, from the respective Ag-Si and Fe-Si phase diagrams. The value of log $\gamma_{Si}^{Ag} = 0.3$ was not considered as reliable however as that calculated from the Fe-Si diagrams as follows.

A liquid solution of $N_{Si} = 0.73$ is in equilibrium with pure solid silicon at 1207°C. Taking the melting point of silicon at 1414°C and its heat of fusion[12] as 11,100 cals/gr atm, these data give $\gamma_{Si}^{Fe} = 0.84$ in the liquid solution at 1207°C. Temperature adjustment was then made using the partial molar heat of solution of silicon[13] in liquid iron giving $\gamma_{Si}^{Fe} = 0.89$

heat of solution of silicon[13] in liquid iron giving $\gamma_{Si}^{Fe} = 0.89$

The composition range of the distribution study extended from $N_{Si} = 0.15$ to 0.55. To bridge the interval between this range and the point $N_{Si} = 0.73$ an extrapolation was made, based on the assumption that log $\gamma_{Si}^{Fe}/(1 - N_{Si}^{Fe})$ is constant. At $N_{Si}^{Fe} = 0.55$ this gave log $\gamma_{Si}^{Fe} = -0.15$, which served to fix the activity coefficient scale.

Values of the activity of silicon dissolved in liquid iron solutions can also be determined from equilibrium data and thus provide a check on the above curve. In particular, data on the solubility of silicon and carbon in liquid iron in equilibrium with graphite

and silicon carbide, were used to calculate the activity of silicon in the binary Fe-Si solution through the free energy change accompanying the formation of silicon carbide.

$$Si_{(l)} + C_{(gr)} = SiC_{(c)} \qquad \ldots\ldots\ldots\ldots \quad (4)$$

Chipman et al[11] determined these solubilities over a range of temperatures, 1200° - 1690°C, and employing the data of Humphrey, Todd, Coughlin and King[7] for reaction (4) calculated a_{Si} in the ternary solution at 1420°C. Correction to the binary solution, i.e. the carbon free solution, was made on the basis that $\log \gamma^{c}_{Si} = 5.5N_{C}$.

Here, γ^{c}_{Si} is defined by the relation:- $\gamma^{c}_{Si} = \gamma^{T}_{Si} / \gamma^{B}_{Si}$

where B and T refer to the binary and ternary solutions respectively, at the same mole fraction of silicon. Thus γ^{c}_{Si} represents the effect of carbon on the activity coefficient of silicon.

Values of γ^{c}_{Si} were determined by Chipman et al[11] from the distribution experiments of silicon between liquid Fe-Si-C solutions and Ag-Si solutions. Carbon is also insoluble in silver so it follows from the definition of γ^{c}_{Si} that at equilibrium for a given temperature:-

$$\log \gamma^{c}_{Si} = \log \frac{N^{Ag}_{Si}}{N^{Fe}_{Si}} \text{ (Fe-C-Si)} - \log \frac{N^{Ag}_{Si}}{N^{Fe}_{Si}} \text{ (Fe-Si)} \qquad \ldots\ldots\ldots \quad (5)$$

Values of $\log (N^{Ag}_{Si} / N^{Fe}_{Si})$ for the binary solution are read off from the binary distribution and subtracted from $\log (N^{Ag}_{Si} / N^{Fe}_{Si})$

from the Fe-C-Si distribution data at the same mole fraction of silicon. The difference, $\log \gamma^{C}_{Si}$ can then be plotted against the corresponding mole fraction of carbon.

Chipman et al[11] found that the relationship between $\log \gamma^{C}_{Si}$ and N_C could best be expressed by the linear equation $\log \gamma^{C}_{Si} = 5{\cdot}5\ N_C$. From the solubility data of Chipman et al[11], silicon carbide and graphite coexist in equilibrium with a liquid at 1420°C in which $N_C = 0{\cdot}0105$ and $N_{Si} = 0{\cdot}355$. Combining this with the free energy change in the reaction (4) gives $\epsilon_{Si} = 0{\cdot}046$, hence $\gamma_{Si} = 0{\cdot}130$, in the ternary solution. Correction to the binary solution, as outlined above, gives $\gamma_{Si} = 0{\cdot}113$ at $N_{Si} = 0{\cdot}355$. This point was shown to be in excellent agreement with the curve derived from the distribution data.

As a further check on the activity curve derived from their distribution experiments, Chipman et al[11] calculated a value of $\log \gamma^{O}_{Si}$, from the data of Gokcen and Chipman[14] on the silicon-oxygen equilibrium in liquid iron. They measured the concentrations of oxygen and silicon in liquid iron contained in a silica crucible under a controlled atmosphere of hydrogen and water at temperatures from 1550 - 1650°C. The following equations were used to define the equilibria involved :-

$$SiO_2(s) = Si + 2\,O \quad \ldots\ldots\ldots\ldots \quad (6)$$

$$SiO_2(s) + 2H_2(g) = Si + 2\,H_2O(g) \quad \ldots\ldots\ldots\ldots \quad (7)$$

$$H_2(g) + O = H_2O(g) \quad \ldots\ldots\ldots\ldots \quad (8)$$

Their results for reactions (7) and (8) indicated curvilinear relationships between the activity coefficients of silicon and of oxygen, and the silicon concentration. More recent work by Natoba, Gunji and Kuwana[46] and by Pilley and Chipman[46] has shown that these curvilinear relationships were incorrect and that equilibrium conditions were not attained at concentrations above 0·6 per cent Si in the work of Gokcen and Chipman[44]. Pilley and Chipman[46] compared the three sets of data and confirmed the results of Natoba, Gunji and Kuwana[45], establishing also from the data of Floridis and Chipman[43], on the hydrogen-water equilibrium with liquid iron, the following free energy equation for reaction (8).

$$\log K_8 = -20{,}700/T + 11{\cdot}24 \quad \text{i.e.} \quad \Delta G^\circ_T = 135{,}940 - 51{\cdot}43T$$

When the standard free energy change for reaction (6) is combined with that for the formation of silica (9) and also for the solution of oxygen in iron (10), an equation (11) is obtained which yields the free energy change when liquid silicon dissolves in iron to form the dilute solution of unit activity (1 per cent):

$$Si_{(L)} + O_{2(g)} = SiO_{2(s)} \quad \ldots\ldots\ldots \quad (9)$$

$$O_{2(g)} = 2\,\underline{O}\ [\text{in Fe, 1\%}] \quad \ldots\ldots\ldots \quad (10)$$

$$Si_{(L)} = \underline{Si}\ [\text{in Fe}] \quad \ldots\ldots \quad (11)$$

Conversion of this free energy equation for reaction (11) to a mole fraction basis will then give $\log \gamma^{o}_{Si}$ as a function of temperature. To obtain the free energy change in reaction (10) for the solution of oxygen in liquid iron, Chipman et al[11] took the average of two independent series of results.

Dastur and Chipman[17] determined the equilibrium in the reaction of oxygen in iron with hydrogen gas forming water and from the known free energy of formation of water calculated an equation for the free energy change in (10).

Darken and Gurry[18] studied the reaction :-

$$CO_{(g)} + \underline{O}\ (\text{in Fe, 1\%}) = CO_{2(g)} \quad \ldots\ldots\ldots \quad (12)$$

from 1524° - 1600°C. From the known solubility[19] of the oxide in the metal they established the equilibrium constant and standard free energy change in (12). Combining this with the known[20] free energy of oxidation of CO to CO_2 they obtained an equation for the free energy change in (10). Using these data, Chipman et al[11] obtained for reaction (11)

$\Delta G^{o}_{(a.)} = -28,050 + 5{\cdot}54T$ giving $\log \gamma^{o}_{Si} = -6,100/T + 1{\cdot}21$

Hence at 1420°C $\log \gamma^{o}_{Si} = -2{\cdot}40$.

Direct extrapolation of the distribution data of Chipman et al[11] however, would lead to a much lower value of $\log \gamma^{\circ}_{Si}$ than that calculated so from the above equations. Since there is also no sound theoretical technique for calculating $d \log \gamma_{Si}/d N_{Si}$ at infinite dilution, the problem of extending the distribution curve to obtain $\log \gamma^{\circ}_{Si}$ becomes essentially experimental. The lower part of the binary curve also assumes further importance in the study of the ternary Fe-Si-C solution when high concentrations of carbon are present. Carbon increases the activity of silicon in liquid iron solutions. As the concentration of carbon in the ternary solution increases, the silicon concentration at the same activity decreases. Consequently the study of high carbon concentrations means low silicon concentration and to obtain γ°_{Si} these must be compared with the binary system at the same low mole fractions of silicon. The binary distribution data of Chipman et al[11] only extended down to $N^{Fe}_{Si} = 0.15$ and the proposed extrapolation of the curve to $N^{Fe}_{Si} = 0$ at $\log \gamma^{\circ}_{Si}$ was not satisfactory over such a long interval.

Further uncertainty also existed concerning the calibration of the distribution curve to the proper $\log \gamma_{Si}$ scale. This was based on an extrapolation of the function

$\log \gamma_{Si}/(1 - N_{Si})^2$ between the points $N_{Si} = 0.55$ and $N_{Si} = 0.73$. Values of $\log \gamma_{Si}/(1 - N_{Si})^2$ calculated from the resultant curve however were not constant.

The apparent agreement between the fixed point calculated from the solubility data of silicon and carbon in liquid iron in equilibrium with silicon carbide is also misleading as it depends upon the free energy of formation of silicon carbide which was not reliably established. It also depends on the function γ^o_{Si} which is in fact calculated from the data on the binary curve itself.

Calculation of $\log \gamma^o_{Si}$ from equilibrium data on the silicon-oxygen reaction in liquid iron produced a value for $\log \gamma^o_{Si}$ which could not be reconciled with the direct extrapolation of the distribution data.

Consideration of these facts, shows that in general, values of a_{Si} calculated from the curve could not be taken as trustworthy, until the above uncertainties and discrepancies were resolved. It will be recalled that a large discrepancy existed between the activity values of silica in slags based on the work of Kay and Taylor[5] and those from the results of Chipman et al[6].

The latter workers calculated their values from their experimental data on reaction (2).

$$SiO_{2(slag)} + 2\,C_{(gr)} = \underline{Si} + 2\,CO_{(1\ atm)} \quad \ldots\ldots\ldots (2)$$

With carbon monoxide gas at 1 atmosphere the equilibrium constant in this reaction reduces to $K_2 = a_{\underline{Si}}/a_{SiO_2}$. K_2 was calculated from the thermodynamic free energy data on silica and carbon monoxide. Values of $a_{\underline{Si}}$ in the graphite saturated melts were obtained from the distribution data of Chipman et al[12] on the binary and ternary solutions of Fe-Si and Fe-C-Si. Values of a_{SiO_2} were then calculated from their data on reaction (2).

It is clear that the uncertainties connected with silicon activities calculated from the distribution data could well be reflected in the silica activities and could provide a possible explanation for the discrepancy between these values and those of Kay and Taylor[8]. It therefore was highly desirable that the data from which silicon activities were obtained should be re-examined.

The purpose of the present research was to redetermine the distribution data firstly in the binary liquid iron solution and to extend it to the lowest possible values of $N_{\underline{Si}}$ thereby permitting a more accurate extrapolation to $\log \gamma^{o}_{\underline{Si}}$. The

ternary distribution curve could then be extended to include higher values of the carbon concentration corresponding to the lowest silicon concentrations. In calculating the function $\log \gamma^{C}_{Si}$ the values of $\log \gamma_{Si}$ in the binary Fe-Si solutions would then be known at the appropriate low values of N_{Si}.

A further and important purpose of this research was to fix the scale of $\log \gamma_{Si}$ on a more reliable basis. To this end, a study was made of the solubility of silicon in liquid silver in equilibrium with silicon carbide and also with silicon nitride. The activity of silicon in the liquid silver solution could then be obtained through the free energy change accompanying the dissociation of both silicon carbide and silicon nitride. γ^{Ag}_{Si} could thus be obtained from the measured silica solubility values and used to calibrate the curve of $\log \gamma^{Fe}_{Si}$ from the distribution data.

It had been previously pointed out by Kay and Taylor[2] that an error in the free energy change for β-quartz could account for the discrepancies in the silica activity values and in the associated heat of formation of silicon carbide. But in view of the apparent reliability of the data on the heat of formation of silica, it did not then seem probable that this was the cause.

Later, during the course of this research, this was also pointed out by Chipman[21] who referred in particular to the work of Ramsted and Richardson[22] in the following equilibria

$$SiO_2(c) + H_2(g) = SiO(g) + H_2O(g) \quad \ldots\ldots\ldots \quad (13)$$

$$Si(c) + SiO_2(c) = 2SiO(g) \quad \ldots\ldots\ldots \quad (14)$$

Their data on these reactions combined with the known free energy of formation of H_2O[20] leads to a value of the free energy of formation of silica which is approximately four K cals. more negative at 1700°K than the values for SiO_2 in Coughlin's[6] tables.

These observations have been confirmed experimentally by three independent re-determinations of the heat of formation of silica.

Cochrane and Foster[24] calculated a value of -215.6 ± 2.2 Kcals. from effusion measurements made on the reactions between liquid gallium and quartz and also gallium and magnesium oxides. W.A. Good[25] measured the heat of formation of aqueous fluosilicic acid in a rotating bomb calorimeter by burning mixtures of silicon and polyvinylidene fluoride in oxygen in the presence of aqueous HF, giving fluosilicic acid in excess HF solution. Combining the measured heat of this reaction with the heat of solution of silica in aqueous HF solution, reported

by King[27], gives for the heat of formation of silica a value of -217·5 ± 0·5 K cals.

This value is also in close agreement with that obtained by Wise, Margrave, Feder and Hubbard[26] who measured the heats of the following reactions in a fluorine bomb calorimeter.

$$Si(c) + 2F_2 = SiF_{4(g)} \qquad \Delta H_1$$

$$SiO_2(c) + 2F_2 = SiF_{4(g)} + O_{2(g)} \quad \Delta H_2$$

from which

$$Si(c) + O_{2(g)} = SiO_{2(\alpha,c)} \qquad \Delta H_f = \Delta H_1 - \Delta H_2$$

They obtained $\Delta H^\circ_{f298\cdot15} = -217\cdot75 \pm 0\cdot34$ Kcals/mole

These experiments confirmed the suspicions of Kay and Taylor[2] and Chipman[21] and lead to the revision of the accepted value for the heat of formation of silica.

The results of Kay and Taylor[2] on reaction (1) for pure silica, can now

$$SiO_2 + 3C = SiC + 2CO \quad \ldots\ldots\ldots \qquad (1)$$

be used in conjunction with the known free energy of formation of carbon monoxide[6] and the corrected value for silica to give a reliable value for the free energy of formation of silicon carbide. This in turn, permits calculation of the value of $\log \gamma^{Ag}_{Si}$ through the solubility dataon silicon in liquid silver

in equilibrium with silicon carbide. Hence, there is provided a reliable basis for calibrating the curve of log γ_{Si}^{Fe} obtained from the present distribution experiments. The redetermined silicon activities in the ternary Fe-C-Si solutions can thence be employed in recalculating silica activities in slags from the data of Langenberg and Chipman[8].

CHAPTER II

EXPERIMENTAL APPARATUS AND PROCEDURES

CHAPTER II - EXPERIMENTAL APPARATUS AND PROCEDURES

A detailed account of the experimental techniques and apparatus used in this research will be given in this chapter. The work is described in two sections.

In Section I a description is given of the apparatus and procedures adopted in carrying out experiments on the silicon distribution between iron solutions and silver. This is followed by accounts of the experimental work on the silicon carbide and silicon nitride equilibria with liquid silver silicon solutions. Since the results obtained from the silicon nitride equilibrium experiments were contrary to what was expected from the thermodynamic data on silicon nitride, and appeared to have been influenced by some, as yet, unknown physical factors, they are also discussed in this section and are not further considered later.

The reliability of the experimental results from the distribution experiments depends critically upon the accuracy of the chemical analyses determining the concentrations of silicon in each phase. Standard methods for measuring the concentrations of carbon and silicon in iron samples are readily available from the literature. No such method however could be found for the analysis of silicon in silver.

Consequently, a large proportion of the work in this research was devoted to the development of techniques capable of measuring concentrations of silicon in silver as low as 0·001% Si. This work is fully described in section II of this chapter.

SECTION I EXPERIMENTAL APPARATUS AND PROCEDURE

Distribution Experiments

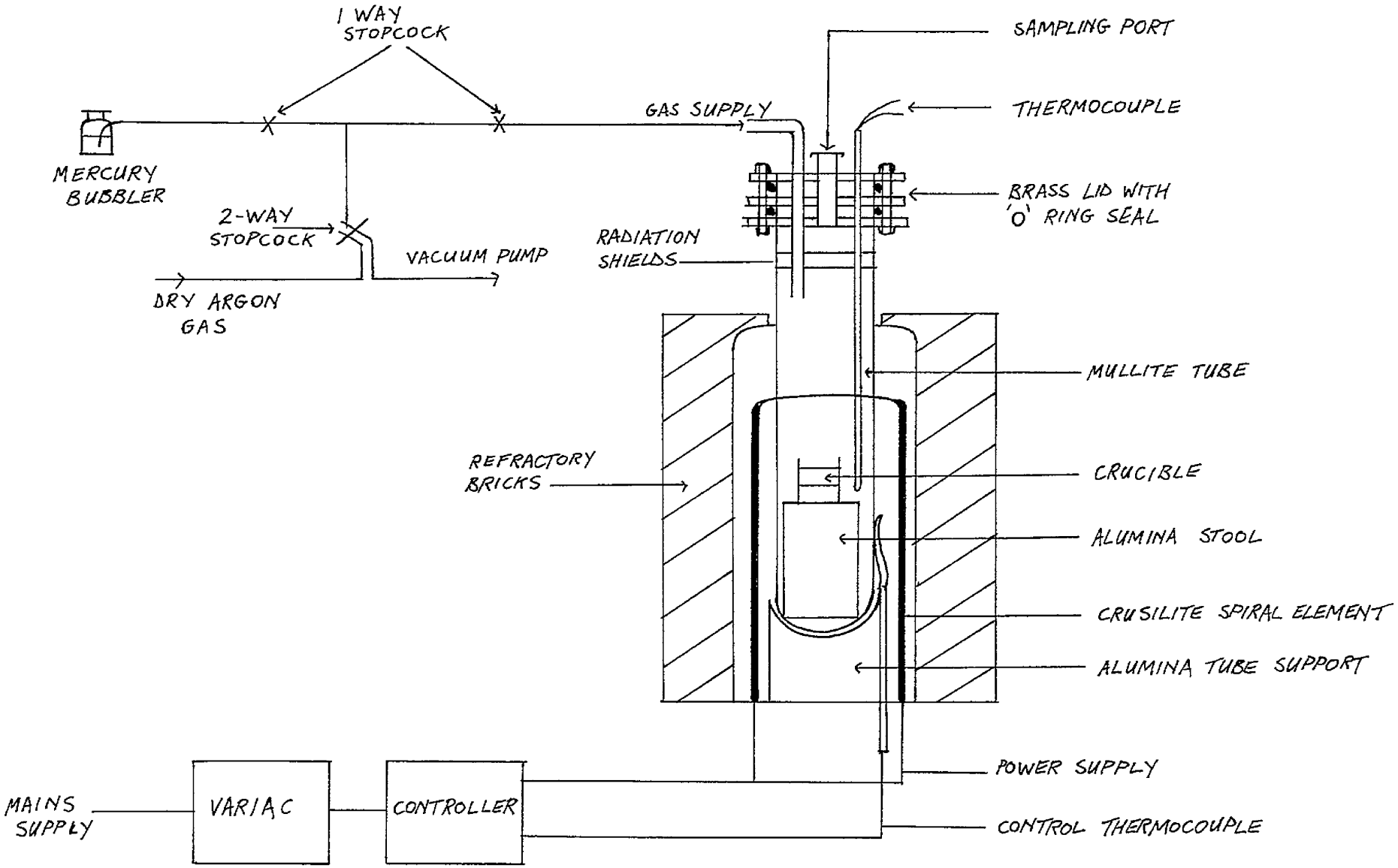
The relatively simple furnace arrangement shown in Fig [I] was used in the distribution studies.

The furnace itself was resistance heated. It consisted of a spiral silicon carbide element centrally positioned within a square 'sindanyo' box and surrounded by refractory brickwork.

The 1.1/2" diameter, mullite reaction tube was supported by an alumina stool and stood concentrically within the spiral element. Since mullite and silicon carbide fuse at high temperature, care had to be taken to ensure no contact between the tube and the element. A refractory thermocouple sheath was cemented to the supporting alumina stool so that it stood between the element and reaction tube with its tip at the centre of the furnace hot zone.

The "crusilite",(SiC), element provided a 2"long zone, with a 5°C temperature gradient from middle to end, inside the

FIG. 1


1 WAY STOPCOCK
SAMPLING PORT
GAS SUPPLY
THERMOCOUPLE
MERCURY BUBBLER
BRASS LID WITH 'O' RING SEAL
2-WAY STOPCOCK
RADIATION SHIELDS
VACUUM PUMP
DRY ARGON GAS
MULLITE TUBE
REFRACTORY BRICKS
CRUCIBLE
ALUMINA STOOL
CRUSILITE SPIRAL ELEMENT
ALUMINA TUBE SUPPORT
POWER SUPPLY
MAINS SUPPLY
VARIAC
CONTROLLER
CONTROL THERMOCOUPLE

mullite tube at 1500°C. Temperature control was effected by means of an electronic, mercury switch relay controller, sensitized by a thermocouple in the sheath between the element and tube. Another thermocouple, introduced into the furnace tube in a mullite protective sheath, indicated the hot zone temperature within the tube and this remained constant to ± 2°C at 1500°C.

Both thermocouples were of the Pt/13% Rh.Pt type and temperatures were read through a 'Cambridge' millivoltmeter, with the a ppropriate cold junction correction applied. They were calibrated by the melting point method with gold and palladium wires. This was done by connecting the separated thermocouple wires with a thin piece of gold wire. The thermocouple was then slowly heated to the melting point temperature of gold when the wires were severed and the temperature reading noted. A plot of time vs. millivolt reading was used to correct the temperature read for rate of heating. A similar calibration with palladium wire was carried out. The separated thermocouple wires were then fused together in an oxygen enriched coal-gas flame.

The metal charge was contained in a one inch diameter, fused silica, crucible which sat upon alumina stools locating it in the centre of the hot zone.

A brass lid was fitted to the top of the furnace and secured with a vacuum tight seal by two rubber 'O' rings screwed in position between grooved brass rings. Two refractory disks suspended by screws beneath this lid served as radiation shields. The lid was equipped with three inlets. The first admitted the reaction tube's thermocouple sheath. The second was a half inch diameter sampling port and was fitted with a screw cap and sealed with a lead disk. The third provided a connection to the inert gas supply and vacuum pump through polyvinylchloride tubing.

The tubing was connected through vacuum stopcocks to a rotary vacuum pump and a mercury bubbler opening to atmosphere. The inert gas used was argon, dried by passing it through U-tubes containing anhydrous calcium chloride and magnesium perchlorate.

Metals Charge

The iron-silicon alloys used in these experiments were made up from master alloys diluted with the requisite amounts of electrolytic iron powder. The master alloys were prepared by melting weighed quantities of silicon metal and iron powder in an alumina crucible under an atmosphere of flowing hydrogen. The melt was held liquid for fifteen minutes then quickly cooled, removed from the crucible, and crushed to

to a powder in a steel morter.

Iron carbon master alloys were also prepared for experiments on the ternary solutions, (Fe-C-Si). These were made by melting "Armco" iron in an open carbon crucible in the coil of a high frequency induction furnace. The liquid metal was held for about twenty minutes in the crucible then quenched in water, dried, and crushed to a powder in a steel morter. The silicon metal used in these experiments was supplied by the Union Carbide Co and contained on their analysis:- Si 98·69, Al 0·10, Ca 0·01, Fe 0·65. The silver metal was pure granular obtained from Messrs. Johnson, Matthey.

Experimental Procedure

About 50 gr of granular silver and a similar weight of the requisite iron alloys were weighed into a silica crucible and well mixed. The crucible was positioned inside the furnace tube which was then sealed and evacuated by the rotary vacuum pump. It was then tested for leaks. The apparatus was considered sufficiently 'tight' if the pressure indicated on the mercury manometer rose by less than 1 mm in 20 minutes with the rotary pump valved off.

The crucible temperature was next raised to 900°C and allowed to remain steady with the system being continuously

evacuated for several hours - usually overnight. The apparatus was again vacuum tested, as before, and the crucible temperature raised to 1100°C where it was allowed to remain under vacuum for about 15 minutes. This procedure was used to remove residual oxygen dissolved in the silver metal.

The rotary pump was cut off after 15 minutes and dried argon gas admitted to the furnace tube. This was allowed to pass through the apparatus and out to atmosphere through the mercury bubbler for 10 minutes. The furnace temperature was meanwhile raised to 1570°C (1500°C in the ternary experiments). The argon gas flow was stopped after 10 minutes, leaving a stagnent atmosphere of argon inside the furnace tube. The use of a static atmosphere was intended to prevent the introduction during the experiments of traces of oxygen, present in cylinder argon. The metals were then held at temperature for at least five hours before samples were taken from each liquid layer. Samples taken after shorter periods of time, approximately one and half hours, indicated that the time allowed was more than sufficient to attain equilibrium.

In order to sample the melts, the screw cap on the furnace top was removed and argon gas passed rapidly through the tube to prevent oxidation. A glazed silica sampling tube

with an attached aspirator bulb was thrust quickly to the bottom of the crucible and a sample withdrawn from the lower layer of silver solution. An iron layer sample was then immediately obtained in the same manner. These samples were quickly cooled by quenching in water. The silver samples were buffed to remove traces of silica adhering to their surfaces from the sampling tubes. Crosssectional cuts were then taken for analysis. The complete iron samples were crushed to a fine powder in a steel percussion mortar and the powder then analysed. No evidence of segregation could be seen in these samples. Any samples from either phase which showed the presence of the second phase were rejected.

This procedure was followed for the distribution experiments on both the Fe-Si and Fe-Si-C solutions.

Experimental Study of Equilibrium Solubility of Silicon in Silver

The object of these experiments was to determine the concentrations of silicon in silver solutions in equilibrium with silicon carbide at different temperatures. The furnace arrangement used in the distribution experiments and shown in Fig. [I] was found to be suitable also for the silicon carbide equilibrium work.

The charge of pure silver or silicon silver alloy was placed in a silicon carbide crucible which was positioned on alumina stools inside the furnace tube. A similar procedure to that used in the distribution runs was then followed in bringing the crucible and charge to temperature under a static atmosphere of argon.

The equilibrium can be approached from both directions by using firstly a silicon carbide crucible containing pure silver and secondly a carbon crucible containing a silver silicon alloy.

Early experiments with both types of crucible indicated certain features of this reaction which necessitated slight experimental changes. In the first place the reaction was found to be very slow. In fact at least forty hours are required to reach equilibrium starting from the pure phases. It was also found that during the long period a certain amount of silver was being lost by evaporation from the open crucibles to the cooler parts of the furnace tube.

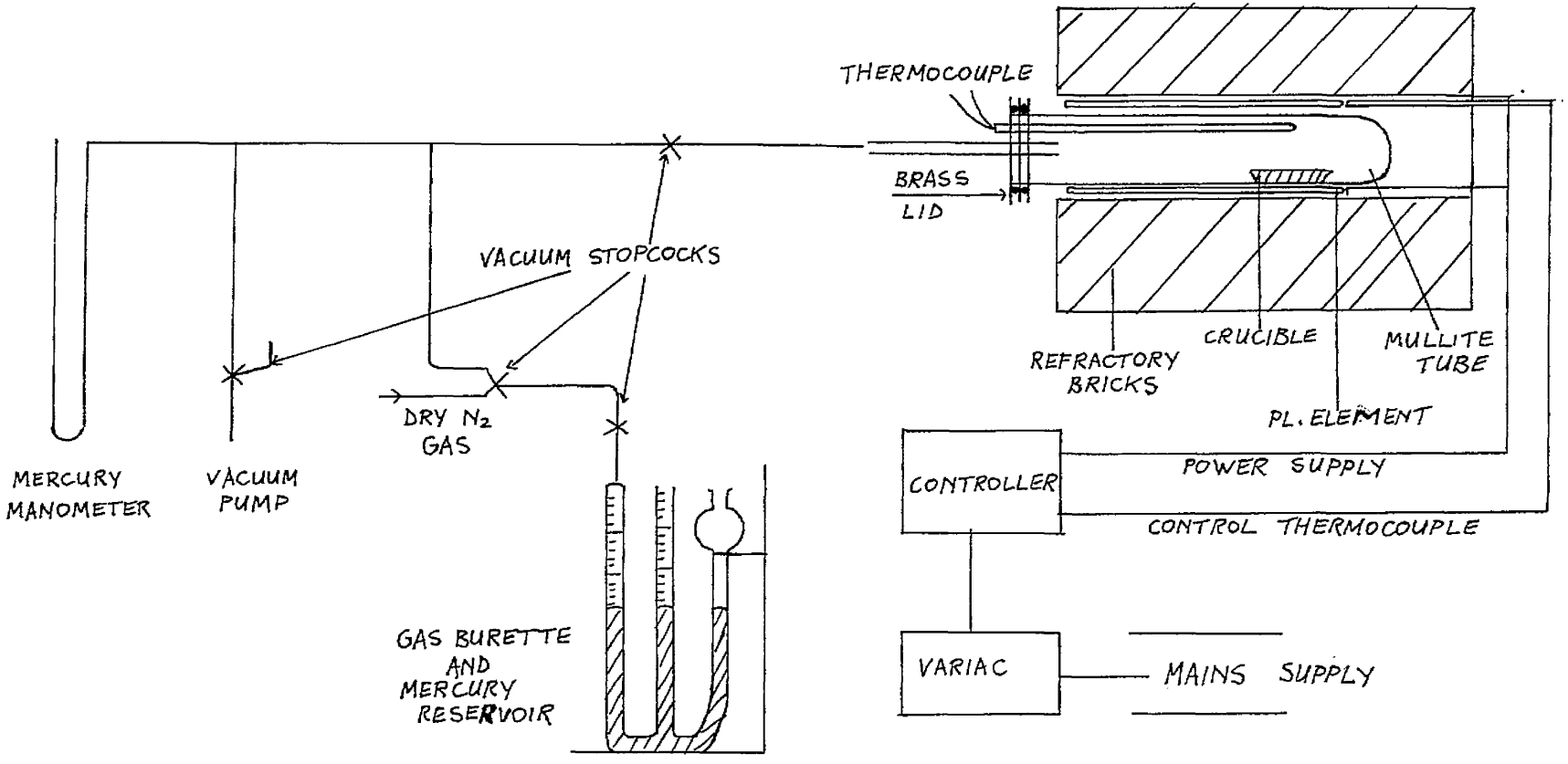
The latter trouble was overcome by fitting a tight carbon lid to the top of the crucibles. Over a period of about fifty hours this lid reduced the loss of silver to about 1% of the total charge. In view of the length of time required for the reaction to reach equilibrium, the error arising from

this source will be considerably less than 1% on the analysed concentration of silicon, and is certainly within the limits of error of the chemical analysis, estimated as ± 2%.

Initially, fairly thick graphite lids were used which introduced sampling problems. Several runs were made without actually sampling at temperature. The crucible was allowed to cool to room temperature and samples were cut from the frozen alloy. The slow reaction rate makes this method reasonably accurate but since it was obviously preferable to sample at temperature another technique was later employed.

To enable a sample to be obtained from the liquid metal charge, the carbon lid was cut as thin as possible and grooved diametrically. When a silicon sampling tube was lightly pressed down on the groove the lid split open allowing the crucible contents to be sampled. This method was successfully used in sampling silver solutions in equilibrium with silver carbide at 1500°C. During sampling, argon gas was passed rapidly through the furnace tube, as in the distribution runs, to prevent oxidation of the silicon in the silver solutions. The samples obtained were quenched in water, dried, buffed, and cut for analysis.

FIG. 11


THERMOCOUPLE
BRASS LID
VACUUM STOPCOCKS
DRY N_2 GAS
MERCURY MANOMETER
VACUUM PUMP
GAS BURETTE AND MERCURY RESERVOIR
REFRACTORY BRICKS
CRUCIBLE
MULLITE TUBE
PL. ELEMENT
CONTROLLER
POWER SUPPLY
CONTROL THERMOCOUPLE
VARIAC
MAINS SUPPLY

Experiments on the Silicon Nitride-Silver Equilibrium

Several experiments were performed on an apparatus constructed for the study of the equilibrium between liquid solutions of silicon in silver and nitrogen gas in forming silicon nitride, according to the reaction,

$$3\,\underline{Si}\ (\text{in Ag}) + 2\,N_2(g) = Si_3N_4(s)$$

An outline of the apparatus is shown in Fig. [II]. The mullite reaction tube is held in a horizontal, platinum wound, resistance furnace. The temperature in the tube was maintained constant to $\pm$ 2°C by an electronic controller operating on the power input to the furnace. The reaction tube was connected by copper tubing to a mercury manometer and a rotary vacuum pump. An outlet from the copper tube was connected through vacuum stopcocks to a graduated glass U-tube with an attached mercury reservoir. High purity nitrogen gas from a cylinder was admitted through a separate vacuum stopcock to the graduated U-tube. Hence by raising or lowering the mercury reservoir, a measured volume of N_2 gas could be admitted to or removed from the reaction vessel. The pressure of known quantities of gas in the reaction tube could then be read on the mercury manometer.

The metal charge was placed in a boat shaped alumina crucible which was partially covered with alumina cement to cut down the loss of silver by evaporation from the crucible. The

melt temperature was obtained by means of a thermocouple introduced into the furnace tube hot zone through a mullite sheath.

Experimental Procedure

A pressure vs. volume curve for the apparatus was first obtained. A charge of pure silver was weighed into the alumina crucible which was then placed in the mullite tube and the apparatus sealed. The crucible temperature was raised to 1000°C under vacuum to remove oxygen and ensure that there were no leaks. The tube was then filled with hydrogen gas and the temperature raised to 1450°C. At temperature the tube was re-evacuated and measured volumes of nitrogen admitted. The pressure on the manometer corresponding to each volume of nitrogen was measured. The readings were checked by withdrawing measured volumes of gas and noting the pressures again. Steady pressures were rapidly attained and ranged from 80 - 1000 mm Hg. The pressure/volume curve for the system with the pure silver was thus obtained.

The same procedure was then followed with charges of silver silicon alloys and in one case pure silicon metal.

Immediate absorption of the nitrogen gas was observed with the liquid silicon charge but disappointing results were

obtained with the silver silicon solutions and experimental problems became apparent. From the data of Elliot and Pehlke[28] on the reaction with liquid silicon, the equilibrium nitrogen pressure at 1450°C is about 2 mm Hg. over liquid silicon. In a typical experiment of the present work, 20 gr of a silicon solution in silver of $N_{Si} = 0.13$ absorbed 10 ccs of N_2 gas (measured at room temperature and pressure) at 1450°C., over one hour. No further absorption was observed although the nitrogen pressure was varied from 30 mm to 1000 mm Hg.

The activity of silicon in the solution can be calculated using the value $\gamma_{Si} = 1.15$ obtained from the silicon carbide reaction results of the present work. Hence the equilibrium nitrogen pressure over this solution can be estimated to be about 20 mm. A much greater absorption of nitrogen should therefore have been observed.

An important experimental difficulty was also encountered. The evaporation of silver from the solution reduced the weight of the charge by 7.5 gr so that the concentration of silicon after 1 hour rose to $N_{Si} = 0.25$. The corresponding reaction pressure for this solution is about 13 mm. This evaporation of silver from the solution is greatly increased at lower pressures so that conditions at low pressures (30 mm Hg) make this method of studying the reaction impractical.

There is, however, no obvious reason for the very small absorption of nitrogen which was found, especially since a very rapid absorption is observed with liquid silicon. It is possible that the reaction is self inhibited by the formation of a thin film of silicon nitride across the surface of the solution. A similar effect would be caused by a layer of silica, but none was definitely observed on the surface of the frozen alloy. Precautions were taken to exclude all oxygen from the system including prolonged flushing with hydrogen.

In view of the nature of the results found in these experiments, no great significance can be ascribed to the small absorptions which were observed. No further work was carried out on this reaction.

SECTION II CHEMICAL ANALYSIS

Analysis of Silicon in Silver

Two reliable methods were developed for this analysis. Unfortunately, the first method could not be extended to concentrations below 0·05% Si, so the second method was used for concentrations<0·05%. Analyses of the same sample done by each of the two methods were in excellent agreement and provided a useful check on their reliability. Method one is an adaptation of a method used for analysing silicon in copper-silicon alloys and is outlined below after A.S.T.M. 1956 Methods of Chemical Analysis of Metals.

Principle of Method I

A slightly acid solution of silica or fluosilicic acid when treated with xs ammonium molybdate solution forms yellow-green molybdisilicic acid. Photometric measurement is made at 435 mμ.

Concentration Range

Recommended concentration range is from 0·04 - 1·00 mg of Si in 100 ml of solution using a cell depth of 1 cm. Sample weight should not exceed 0·5 gr of silver alloy.

Colour Stability

Full colour develops in 10 minutes and fades gradually. A uniform time for colour development should be used for both calibration solutions and samples.

Interferences

The solutions must be free from anions which give insoluble silver salts as these produce erroneous readings on the spectrophotometer. Solutions showing any opalescence must be rejected. Phosphorus > 0·05 mg in the final solution also forms phosphomolybdic acid. In the presence of xs. nitric acid small amounts of HF used to dissolve the silicon are soluble in the final solution. No trouble arose from any nitrites which were possibly present although no urea addition was made since this invariably gives rise to a precipitate.

Apparatus

(a) Unicam Spectrophotometer S.P. 600. (b) Platinum crucibles with lids. (c) Plastic Reagent bottles - 500 ml capacity, Pyrex volumetric flasks and plastic funnels.

Reagents

(1) Silver - pure bar or grain.

(2) Saturated Boric acid solution. About 60 gr/litre dissolved hot and cooled.

(3) Standard Silicon solution. (1 ml = 0·040 mg Si)

0·0856 gr of pure anhydrous silica are fused with 1 gr anhydrous

Na_2CO_3 in a platinum crucible. The melt is cooled, dissolved completely in water and diluted to 1 litre in a volumetric flask and stored in a plastic container.

(4) Ammonium Molybdate solution. 100 gr of $(NH_4)_6Mo_7O_{24}.4.H_2O$ are dissolved in water and diluted to 1 litre.

Calibration Procedure

8 mls of (1 : 2) HNO_3 solution are added to 0·50 gr of pure silver in a platinum crucible followed by 6 - 8 drops (0·3 - 0·4 mls) of HF solution. The crucible is covered and stood until solution is complete. Solution can be hastened by heating on a hot plate at 60 - 65°C maximum.

The cooled solution is transferred completely to a 250 ml pyrex volumetric flask through a long stem plastic funnel dipping into 25 mls of saturated H_3BO_3 solution previously added to the flask. The solution is made up to 250 mls and well mixed.

20 mls of this solution are transferred to each of 6, 100 ml pyrex, volumetric flasks. 2 mls (1·2) HNO_3 solution are then added and the volume brought up to 50 mls. Zero, 5, 10, 15, 20, 25 ml portions of standard Si solution are added respectively to the six flasks. 5 mls of ammonium molybdate solution are then added and the solution made up to 100 mls. After full colour development, a portion is transferred to a clean, dry, absorption cell and its transmission density read at 435 mμ.

The spectrophotometer is 'zeroed' against a 1 cm cell containing distilled water used in the analysis. The reading on the cell containing no silicon solution is taken as the reagent blank and is subtracted from each of the other cell readings.

Sample Solution

0.50 gr of sample is weighed into a Platinum crucible followed by 6 mls (1.2) HNO_3 solution and 6 - 8 drops (0.3 - 0.4 mls) HF solution. The crucible is covered and stood until solution is complete. Gentle heating may be required to aid the solution of the sample. Overheating may result in loss of silicon by volatilization as silicon fluoride.

The cooled solution is added to a 250 ml pyrex volumetric flask through a long stem plastic funnel dipping into 25 mls of H_3BO_3 solution previously added to the flask. The solution is made up to the mark and well mixed. Equal volumes containing a suitable amount of Si to give a reading on the calibration curve are added to two 100 mls pyrex volumetric flasks. 2 vols of (1.2) HNO_3 are added to each portion. One portion is used for background colour and the other treated with ammonium molybdate solution (as for calibrations) and its absorption reading taken. After subtraction

of the 'blank' reagent reading, reference to the calibration curve will give the concentration of silicon in the final solution and the percentage present in the sample may then be calculated.

The method as outlined has a lower limit on this calibration of 0·2% Si in silver. By using a dilution of 40 - 100 mls in the final solution with suitable calibration and making the lowest point on the calibration curve correspond to $2\frac{1}{2}$ mls of standard Si solution, this limit can be extended to 0·05% Si in Ag. This is the lowest concentration which the method can handle without serious loss of sensitivity.

During research on the preparation of the calibration curve for this method it was found that serious pick-up of silicate could occur in the solutions from soft glass-ware such as the volumetric flasks and containers for the standard solutions. Plastic containers are therefore used for holding standard solutions and all glassware used was of the 'Pyrex' type. This rendered silicate pick-up from containers negligible.

The saturated boric acid solution in the 250 mls standard flask complexes with the xs HF acid in the initial acid solution and prevents attack on the glassware which is protected from splashes by the long stem funnel.

Attempts to extend this method to lower values of

silicon in silver were unsuccessful. Dilution of the calibration solution to give the required amount of silicon corresponding to 0.5 gr silver sample resulted in a complete loss of sensitivity. A similar effect was obtained on increasing the weight of silver. This latter method is restricted by the limited solubility of silver molybdate and could not be extended sufficiently to permit the required analysis.

A suitable linear curve is obtained from the diluted silicate calibration solutions which have been simply acidified and treated with ammonium molybdate. Experiments were therefore carried out using a variety of techniques to find a method for giving a complete separation of the silicon from the silver. These methods are mentioned here and the possible reasons for their failure in most cases.

(1) Separation by precipitation of silver as silver chloride. This was examined using both hydrochloric acid and sodium chloride. Urea was also added to remove nitrites. Absorption readings on the resulting solutions were irregular and had no apparent relation to the silicate concentration. Careful hot leaching of the precipitate, etc. made no difference. The absorption readings appeared to indicate that the silicate ions were being occluded in the chloride precipitation. The presence of both chloride and nitrate ions in the solution also raised the absorption of the solution making the sensitivity too low for

these concentrations at the appropriate wavelengths.

(2) Extraction of the silver as the dithizone complex in carbon tetrachloride was also attempted. The extraction proved impractical due to the large volumes of extractant required to remove the silver and the slowness of the procedure. The silver molybdate complex can be extracted into butanol from its aqueous solution so a set of standard solutions were shaken up with butanol and the absorption readings in the butanol solutions taken. Very high blank readings were found and the absorption of the silicate solutions did not appear to obey Beer's law.

(3) The removal of silver from the solution electrolytically also resulted in erratic absorption readings on the remaining silico-molybdate solution. Electrolysis of the silver from alcoholic, ammoniacal solution on to Platinum electrodes was attempted but produced a grey sludge which was subsequently filtered. Readings on the acidified solutions were erratic. Electrolytic separation of the silver by the mercury-cathode technique could not be done in solutions containing nitric acid since this dissolves the mercury. Silver only dissolves in concentrated boiling sulphuric acid and difficulties arise in the subsequent dilution and control of the pH in the resulting solutions so that samples could not be easily dissolved by this solvent for a later electrolytic separation.

(4) The method of separation which was eventually found to be suitable consisted of extracting the silicon as silicate from the silver sample by melting the sample under sodium carbonate and leaching the fused mass with hot distilled water. Silver is insoluble in the carbonate melt and so is easily and completely separated. The sample is melted at 1000°C in a 'muffle' furnace under oxidising conditions so that the silicon is oxidised to silica which is insoluble in silver and dissolved in the carbonate melt. Since silver alloys with platinum and iron is fairly soluble in fused carbonate, nickel crucibles were used to hold the melt. Some nickel does dissolve in the melt especially if the crucible has been in use for a number of times so tartaric acid (1%) is added to the sulphuric acid solution used to acidify the alkaline extract from the melt. The faint green nickel carbonate colour of the alkaline solution is discharged on acidification. The nickel crucibles are fitted with lids to prevent undue evaporation of the melt and crucibles are held at temperature in the furnace for a uniform time of ten minutes. It was found that erroneous results arose from holding the crucibles at temperature over long and varying periods.

The method of this analysis is outlined for convenience as follows after the manner of Method I.

Method II used to determine % Si in Silver for % Si 1%

Principle of the method

An acid solution of silicic acid when treated with excess ammonium molybdate solution forms yellow-green molybdisilicic acid which obeys Beer's Law. Photometric measurement is made at 420 mμ.

Concentration Range

The concentration range on the standard curve for this method is from 0·05 - 0·50 mg of silicon in 100 mls of solution using a cell depth of 2 cm.

Colour Stability

Full colour develops in just under 10 minutes and gradually fades. It is necessary to use a uniform time reading for both calibration and sample solutions. In this instance readings were taken after 10 minutes.

Apparatus

(a) Unicam Spectrophotometer S.P. 600.

(b) Nickel crucibles fitted with lids approximately 70 mls capacity.

(c) Plastic filter funnels and plastic bottles 500 ml - 1000 mls respectively. Pyrex 100 ml volumetric flasks.

Reagents

(1) Standard Si Solution (1 ml = 0·040 mg Si)

0·042 gr of anhydrous SiO_2 is fused with 1 gr anhyd. Na_2CO_3 in a platinum crucible. The cooled melt is completely dissolved in dist. water, diluted to 500 mls in a standard pyrex flask, and transferred immediately to a plastic bottle.

(2) Ammonium Molybdate Solution

About 100 gr of $(NH_4)_6Mo_7O_{24}.4H_2O$ is dissolved in water and the solution decanted at once into a plastic bottle.

(3) Sulphuric Acid-Tartaric Acid Solution

To 5 gr of tartaric acid dissolved in water are added 50 mls of conc. sulphuric acid and the whole made up to 500 mls and transferred to a plastic bottle.

Preparation of Calibration Curve

1 gr of pure silver plus 2 gr of anhydrous Na_2CO_3 are transferred to each of six nickel crucibles. The crucibles are covered and placed in a muffle furnace at 1000°C for exactly 10 minutes. After removal from the furnace and cooling to room temperature, approximately 20 mls of dist. water are added to each flask followed by 2·0, 4·0, 6·0, 8·0, 10·0 ml portions of standard silicon solution to five of the crucibles. The crucible to which no silicon solution has been added is taken as the 'blank' solution.

The solutions are warmed on a hot plate until the carbonate melt has completely dissolved and are then filtered into 100 mls pyrex volumetric flasks using plastic filter funnels and Whatman No. 531 filterpaper. 15 mls of the sulphuric-tartaric acid solution are added at once to each of the flasks followed by 5 mls of the ammonium molybdate solution. The solutions are diluted to 100 mls and stood for 10 minutes. An absorption cell filled with distilled water is used as a reference solution with the photometer set at a light band centred at 420 mμ. Photometric readings are then taken on each of the six solutions. The blank reading is subtracted from each of the calibration solutions. The resultant readings of the calibration solutions are then plotted against mg of Si per 100 mls of solution.

Procedure for Alloys of Silicon in Silver

A portion of the alloy sufficient to give from 0·04 - 0·5 mg of Si in the final solution is transferred to a nickel crucible. Thereafter the procedure is identical to that given for the preparation of the calibration solutions except that no silicon solution is added to the crucible.

The percentage of silicon in silver which can be estimated by this method depends on both the range of the absorption curve and the size of the initial sample taken.

In this work the maximum size of sample used was 6 gr with 2 gr of Na_2CO_3 in the nickel crucible. The lower limit on the curve is equivalent to 1 ml of standard Si solution containing 0·042 mg of Si giving the lowest percentage of 0·0007% which sufficed for the analyses in this research. It may be possible to lower this limit by concentrating the alkaline extract solution obtained initially from the sample, provided a reasonably low blank is also obtained to keep the sensitivity to a proper level.

For the analysis of samples containing higher percentages of silicon, say, > 1% Si., the sample weight taken can be lowered and the initial extracting solution diluted to permit using the spectrophotometric method. Otherwise a standard gravimetric method for silicate can be applied to the alkaline silicate solution.

Analysis of % Si in Fe-Si samples

Since the % Si in the iron samples to be analysed all contained at least 1·0% silicon it was decided that a gravimetric method would be accurate enough. Since silver is slightly soluble in liquid iron and small traces could appear in the iron phase samples, sulphuric acid was chosen as the solvent in this method to obviate the possible contamination of the silica precipitate with silver chloride. The following

procedure was used for the analysis, of Vogel[80].

1 gr of sample is weighed into a 600 ml pyrex beaker followed by 50 mls of (1•1) H_2SO_4 solution which is boiled until the sample is dissolved. For high carbon samples approximately 5 mls of conc. HNO_3 solution are added to assist in oxidising the carbon and dissolving the sample. 100 mls of (1•8) H_2SO_4 solution are then added to the beaker and the solution evaporated to fumes of sulphur trioxide. Approximately 200 mls of (1•8) H_2SO_4 are then added to the beaker. Sputtering is avoided here by slow and careful pouring of the H_2SO_4 solution steadily down the wall of the beaker. The solution is then strongly boiled until all the iron salts are redissolved. It is then immediately filtered (hot) through an ashless, paper pad in a Gooch crucible, and washed alternately with hot dil. H_2SO_4 and hot distilled water. The pad and precipitate are transferred to a weighed platinum crucible, dried slowly, ignited to burn off carbon, and placed in a 'muffle' furnace at 600°C. for 15 - 30 mins. The crucible is cooled in a dessicator and quickly weighed. About 0•5 mls (1•1) H_2SO_4 is added to moisten the residue followed by 3 - 5 mls of analar, grade, concentrated Hydrofluoric acid. The solution is carefully evaporated until no more fumes of SO_3 are evolved, the crucible replaced in the furnace at 1100°C for 15 mins, removed,

cooled in a dessicator, and reweighed. The loss in weight represents silica from which the % Si in the sample is calculated. The filtrate and washings were transferred to a pyrex beaker and evaporated to about 50 mls. Conc. HCl acid solution was added to test for silver. In general, the silver concentration was found to be irregular from zero to about 3% in a very few cases.

Analysis of % C in Fe-C-Si Samples

This analysis was performed on samples from the ternary distribution experiments by means of the standard[29] combustion method for carbon in steels. The carbon of the sample is oxidised in a stream of purified oxygen gas at 1100°C and the carbon dioxide absorbed in a weighed bottle containing soda-lime absorbent. The weight of carbon dioxide gas thus found gives the % C of the sample. The absorption apparatus was checked before and after each set of carbon analyses against standard samples containing 3·00 and 0·15% carbon.

C H A P T E R III

EXPERIMENTAL RESULTS

TABLE I - EXPERIMENTAL RESULTS

Distribution of Silicon between the liquids Iron and Silver

Run No.		Iron Phase		Silver Phase		
		%Si in Fe	N_{Si}^{Fe}	%Si in Ag	N_{Si}^{Ag}	$\log \frac{N_{Si}^{Ag}}{N_{Si}^{Fe}}$
+ B	4	7·26 7·20	0·155	0·0168 0·0183	0·000870	-2·30
B	9	6·04 6·86	0·126	0·0110	0·000464	-2·44
B	6	3·61 3·75	0·071	0·00333 0·00363 0·00436	0·000145	-2·69
B	7	4·10 4·15	0·070	0·00250 0·00272 0·00362	0·0001136	-2·84
B	8	2·05 2·13	0·041	0·00103 0·00150	0·0000562	-2·94
B	10	7·07 7·10	0·132	0·0110 0·0135	0·000488	-2·43
B	11	2·54 2·46	0·049	0·00150 0·00130	0·0000569	-2·93
+ C	1	22·16 21·70	0·359	0·41 0·49	0·01713	-1·32
C	2	19·06 19·00	0·319	0·54 0·54	0·02045	-1·19
C	3	19·40 19·05	0·321	0·39 0·39	0·01484	-1·34
C	4	19·55 20·30	0·331	0·50 0·53	0·01955	-1·33

NOTE + Runs marked B were performed at 1570°C and those marked C at 1450°C.

The mole fractions N_{Si}^{Fe} and N_{Si}^{Ag} are calculated from the mean percentage analysis in each case.

TABLE II Distribution of Si between liquid Silver and liquid Fe-C Solutions. 1500°C

Run No.		Iron Phase				Silver Phase		$\log \frac{N_{Si}^{Ag}}{N_{Si}^{Fe}}$
		%Si	%C	N_{Si}	N_C	%Si	N_{Si}	
T	1 +	3·27 3·12	3·28 3·28	0·0553	0·132	0·00661 0·00640	0·000251	-2·34
T	2 +	3·28 3·12	3·55 3·48	0·0553	0·142	0·00856 0·00844	0·000328	-2·23
T	3	1·94 1·97	3·61	0·0338	0·145	0·00535 0·00682	0·000235	-2·16
T	4	2·94 2·87	2·74 2·77	0·0512	0·114	0·00418 0·00422	0·000162	-2·50
T	5	1·93 1·92	2·26 2·26	0·0340	0·0946	0·00376	0·000145	-2·38
T	6	2·05 2·07	2·54 2·51	0·0369	0·105	0·00284	0·000109	-2·53
T	9	2·85 2·91	3·02 2·99	0·0505	0·122	0·00540 0·00522	0·000204	-2·39
T	11	3·11 3·09	2·51 2·54	0·0552	0·105	0·00963 0·00942	0·000367	-2·16
T	12	3·94 3·92	2·23 2·20	0·070	0·092	0·00580 0·00570	0·000221	-2·50
T	13	2·02 1·98	1·57 1·55	0·0370	0·0674	0·00123 0·00235	0·0000689	-2·73

Continued

TABLE II (CONTD)

Run No.	Iron Phase %Si	Iron Phase %C	Iron Phase N_{Si}	Iron Phase N_C	Silver Phase %Si	Silver Phase N_{Si}	$\log \frac{N_{Si}^{Ag}}{N_{Si}^{Fe}}$
T 14	2·03 2·06	3·35 3·34	0·0355	0·136	0·00292 0·00303	0·000115	-2·49
T 15	3·09 2·93	2·02 1·98	0·0542	0·0650	0·00687 0·00646	0·000259	-2·32
T 16	2·06 2·01	2·79 2·74	0·0363	0·115	0·00315 0·00345	0·000127	-2·45
T 17	1·80 1·83	3·25 3·25	0·0318	0·133	0·00432 0·00412	0·000163	-2·29
T 18	2·10 2·14	3·48 3·49	0·0365	0·1415	0·00446 0·00486	0·000179	-2·31
T 19	2·05 2·04	3·67 3·68	0·0353	0·1482	0·00494 0·00496	0·000191	-2·27
T 20	1·73 1·67	4·07 4·22	0·0294	0·1675	0·00620 0·00627	0·000239	-2·09
T 21	1·67 1·60	3·70 3·68	0·0283	0·150	0·00390	0·000150	-2·28
T* 22	1·52 1·55	4·27 4·36	0·026	0·171	0·00863	0·000265	-1·96

* The runs marked * are performed at 1570°C.

Ø This run was performed in a high frequency induction furnace under argon over a time of 3/4 hours. The charge was frozen in a stream of hydrogen and the phases separated for analysis.

Silver-Silicon Carbide Equilibrium Experiments

The equilibrium $SiC \rightleftharpoons \underline{Si} + C$ in the presence of silver was approached from both sides by suitable experimental arrangements. The dissociation was studied by holding liquid silver at 1450°C and 1500°C in a silicon carbide crucible under an inert argon atmosphere.

In Experiment I at 1450°C the concentration of silicon in silver was found to be 0·50, 0·51% after 50 hours.

In Experiment II, at 1450°C, after 67 hours chemical analyses on samples were 0·49, 0·49, 0·54% Si in silver.
Hence equilibrium concentration at 1450°C is 0·50% Si in silver.
At 1500°C after 25 hrs. concentration of Si in silver found was 0·63% ....Exp 3.
" 1500°C " 50 " """ " " " " " was 0·64% ....Exp 4
Equilibrium concentration at 1500°C is 0·64% Si in silver.
The equilibrium in the reverse direction was studied by holding solutions of silicon in silver at 1450°C in graphite crucibles.
The results of these experiments were erratic.
In Experiment I the silicon concentration in silver at 1450°C dropped from 1·3% to 0·15% after 48 hours. This may have been caused by oxidation.

In Experiment II the silicon concentration dropped from 1·5% to 1·14% after 48 hours, then to 1·0% after 52 hours and remained at 1·0% after 57 hours.

In Experiment III, over 140 hours, the furnace being cooled and samples cut from the frozen silver ingot after every 24 hours, at 1450°C the silicon concentration dropped steadily from 1·3% to 0·33%.

These results indicate that equilibrium conditions were not attained.

C H A P T E R I V

COMPARATIVE DISCUSSION OF RESULTS

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To convert the results of the distribution study to the corresponding silicon activity relative to the pure liquid element, the activity coefficient of silicon in the binary silver-silicon solution is first derived from the silicon carbide + silver equilibrium results.

Free Energy of Formation of Silicon Carbide

The free energy change accompanying reaction (4) at high temperatures has been the subject of several experimental studies[9,31] which have

$$SiC = Si_{(L)} + C_{(gr)} \quad \ldots\ldots\ldots (4)$$

unfortunately produced widely disagreeing results. The results of equilibrium studies[1,2] on reaction (1) provide probably the best means of calculating

$$SiO_2 + 3C = SiC + 2CO \quad \ldots\ldots\ldots (1)$$

the free energy change in (4) by making use of the established free energy of formation of carbon monoxide[6] and the recently redetermined value[24,25,26] for silica.

$$Si_{(L)} + O_2(g) = SiO_{2(\beta\ quartz)} \quad \ldots\ldots\ldots (9)$$

$$C_{(s)} + \tfrac{1}{2}O_2(g) = CO_{(g)} \quad \ldots\ldots\ldots (10)$$

The following equations are used for these reactions:-

ΔG° = 146,000 - 81·20 T cals (1705 - 1628°K)....(1)

ΔG° = -226,260 + 47·34 T cals (for β-quartz).....(9)

ΔG° = -27,800 - 20·40 T cals .....(15)

These give for reaction (4) ΔG° = -24,660 + 6·84 T cals

Adjusting the 'entropy' term to fit heat capacity[7] data gives

(1) ΔG° = -26,000 + 6·74 T cals (1705 - 1628°K).

Activity of Si in Silver

Equation (4) can now be used to recalculate γ_{Si} in the silver-silicon binary solution through the relation $G^\circ = RT \ln \gamma_{Si} N_{Si} = RT \ln a_{Si}$. From the present solubility data at 1500°C, N_{Si} = 0·0242. The activity of silicon calculated from the free energy change in reaction (1) is a_{Si} = 0·02620. This gives γ_{Si} = 1·19 hence at 1500° log γ_{Si} = 0·0755. At 1450°C the solubility data give an average value of 0·51% Si in Ag, i.e. N_{Si} = 0·01934. The free energy change in reaction (1) gives a value a_{Si} = 0·0230. Hence γ_{Si} = 1·18 and at 1450°C log γ_{Si} = 0·073. If the variation in chemical analysis (± 3%) is taken as the main factor contributing to experimental error, then in these solutions log γ_{Si} = 0·07 ± 0·02. The results obtained from experiments using graphite crucibles and silver-silicon solutions to approach this equilibrium from the reverse direction, were

inconsistent amongst themselves. In one series the silicon concentration dropped from 1·5% to 1·0% and remained constant at 1·0% for more than 60 hours. In a second series the concentration dropped steadily from 1·3% to 0·33% over 140 hours. The reasons for these results are not clear but several factors can be considered which influence this reaction. For example, the rate of reaction might be very slow indeed, the silver solutions do not 'wet' the graphite crucible which results in poor contact between the reacting phases, the initial layer of silicon carbide, formed between the solution and its graphite container, remains adhering to the crucible and prevents further reaction, finally there is always the possibility of oxidation although all possible precautions were taken to prevent this.

D'Entrement and Chipman[31] encountered similar difficulties in their study of this reaction at 1420°C. They used graphite crucibles and introduced fluxes of CaF_2, $FeO - SiO_2$ slag, and $CaO - SiO_2 - Al_2O_3$ slag, to improve contact between the metal and SiC formed. They also found that a long period of time was required to establish equilibrium.

When the result of their solubility study of this reaction is combined with the silicon activity calculated from the above equation for the free energy change in reaction (1), a value of $\log \gamma_{Si}$ is obtained which is in good agreement with those

calculated from the present results. They found at 1420°C silicon carbide is in equilibrium with a silver silicon solution in which $N_{Si} = 0{\cdot}017 \pm 0{\cdot}002$. Hence, using equation (1), $\gamma_{Si} = 1{\cdot}16$ and $\log \gamma_{Si} = 0{\cdot}065$.

Hagor[38] has made a recent study of the silver-silicon phase diagram and from this derived a value of $\gamma_{Si} = 1{\cdot}12$, i.e. $\log \gamma_{Si} = 0{\cdot}05$, assuming that the solution is regular. This also agrees well with the present results although the solution does not exhibit regular behaviour and the calculated value of γ_{Si} would be expected[21] to be slightly low.

The value of $\log \gamma_{Si} = 0{\cdot}07 \pm 0{\cdot}02$ obtained from the present work is thus confirmed by two independent sources.

Activity Coefficient of Silicon in Liquid Iron

When equilibrium is established in the distribution experiments at a given temperature,

(3) $\log N^{Fe}_{Si} \cdot \gamma^{Fe}_{Si} = \log N^{Ag}_{Si} \cdot \gamma^{Ag}_{Si}$ and (3A) $\log N^{Ag}_{Si}/N^{Fe}_{Si} = \log \gamma^{Fe}_{Si} - \log \gamma^{Ag}_{Si}$

At the low concentrations of silicon in silver established in the distribution experiments it has been shown[18] that Henry's Law is obeyed, and the activity coefficient of silicon can be safely assumed to remain constant. Values of $\log \gamma^{Fe}_{Si}$ can now be calculated for each value of N^{Fe}_{Si} from equation (3A) since $\log N^{Ag}_{Si}/N^{Fe}_{Si}$ is known from the distribution results and $\log \gamma^{Ag}_{Si}$

from the silicon-carbide-silver reaction. The analysis figures for the binary distribution runs and values of $\log N^{Ag}_{Si}/N^{Fe}_{Si}$ are shown in Table I. The derived values of $\log \gamma_{Si}$ are shown in Table III. These have been calculated at 1570°C, 1540°C, 1500°C and 1420°C for comparative purposes. Temperature conversions were obtained through the relationship $d \ln \gamma_{Si}/dt = -L_{Si}/RT^2$, the partial molal free energy of silicon in liquid iron being taken from the data of Korber and Oelsen[10] given graphically by Chipman, Fulton, Gokcen and Caskey[11] vide Fig. III.

In Fig. IV $\log \gamma_{Si}$ is plotted against N_{Si} for each of the four temperatures.

In Fig. V the curve at 1420°C has been drawn, and values of $\log \gamma_{Si}$ taken from the data of Chipman, Fulton, Gokcen and Caskey[11] are shown for comparison. Their values of $\log N^{Ag}_{Si}/N^{Fe}_{Si}$ were converted to $\log \gamma_{Si}$ values by the addition of $\log \gamma^{Ag}_{Si} = 0.07$. The curve is essentially linear over the range $N_{Si} = 0$ to 0.4, and extrapolation to $N_{Si} = 0$ gives a value of $\log \gamma^{o}_{Si} = -3.45$ at 1420°C. Chipman[21] estimated a value of $\log \gamma^{o}_{Si} = -3.4$ at 1420°C. A comparison of the points obtained by Chipman, Gokcen, Fulton and Caskey[11], and those from the present work in Fig. V shows that both are in good agreement. The points, however obtained by Chipman et al[11] all lie below the drawn curve but in fact a line drawn through

Variation in $\log \gamma_{Si}$ with Temperature - Table III

N_{Si}^{Fe}	$-\log \frac{N_{Si}^{Ag}}{N_{Si}^{Fe}}$	$-\log \gamma_{Si}$			
	1570°C	1570°C	1540°C	1500°C	1420°C
0·041	2·94	2·87	2·93	3·00	3·17
0·040	2·93	2·86	2·92	2·99	3·16
0·079	2·84	2·77	2·83	2·90	3·07
0·071	2·80	2·82	2·88	2·95	2·92
0·126	2·44	2·37	2·43	2·50	2·67
0·132	2·43	2·36	2·40	2·46	2·66
0·135	2·30	2·25	2·31	2·38	2·55
	1450°C				
0·359	1·32	1·11	1·14	1·21	1·26
0·319	1·19	0·98	1·01	1·08	1·16
0·321	1·26	1·13	1·16	1·23	1·31
0·331	1·33	1·12	1·15	1·22	1·30

Experimental values of $\log N_{Si}^{Ag}/N_{Si}^{Fe}$ have been converted to values of $\log \gamma_{Si}$ and adjusted to the four different temperatures shown by means of the relationship $d \ln \gamma / dT = - L_{Si}/RT^2$

FIG. III

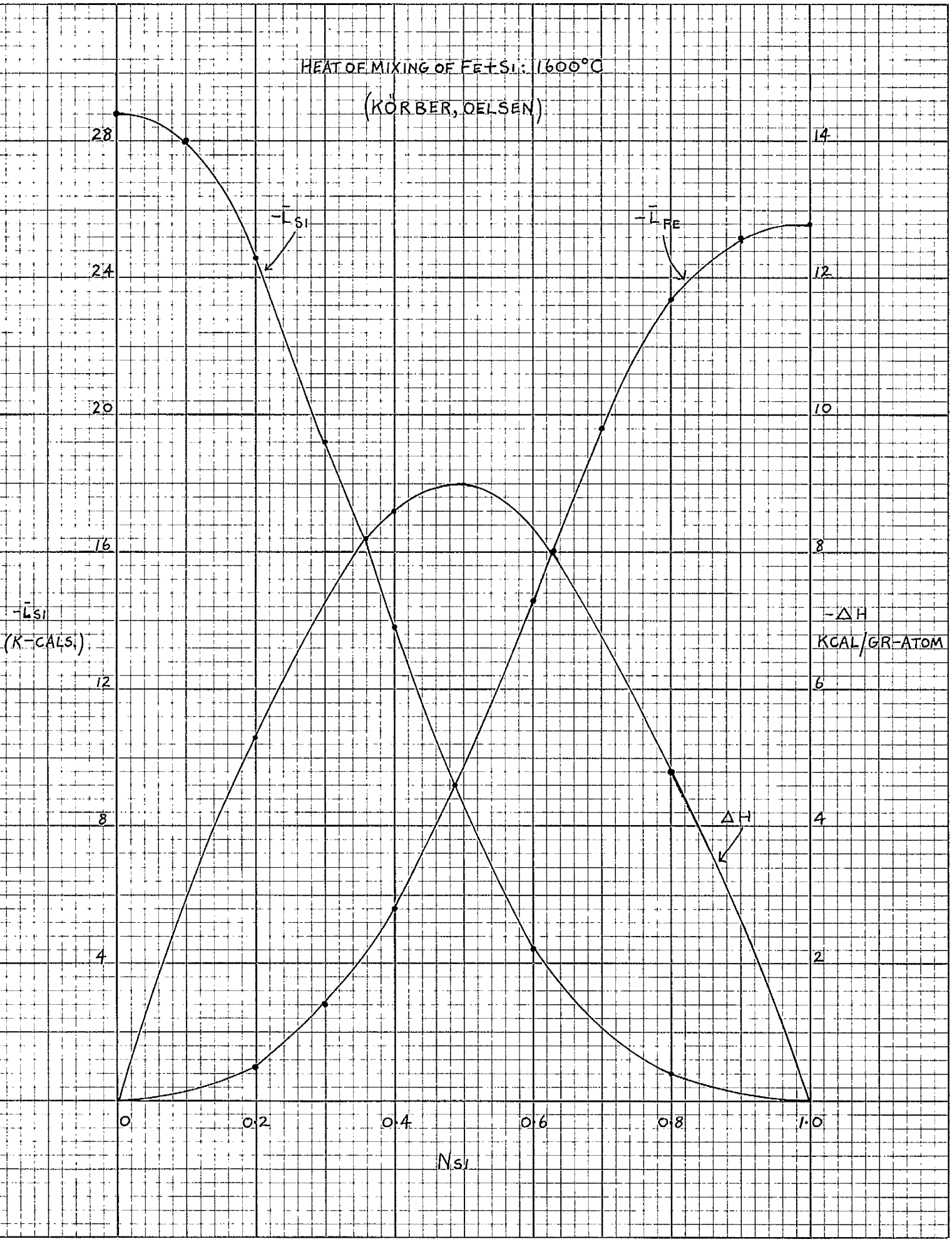

HEAT OF MIXING OF Fe+Si: 1600°C
(KÖRBER, OELSEN)
$-\bar{L}_{Si}$
$-\bar{L}_{Fe}$
ΔH
$-\bar{L}_{Si}$ (K-CALS.)
$-\Delta H$ KCAL/GR-ATOM
N_{Si}
0
0·2
0·4
0·6
0·8
1·0
4
8
12
16
20
24
28
2
4
6
8
10
12
14

FIG. IV

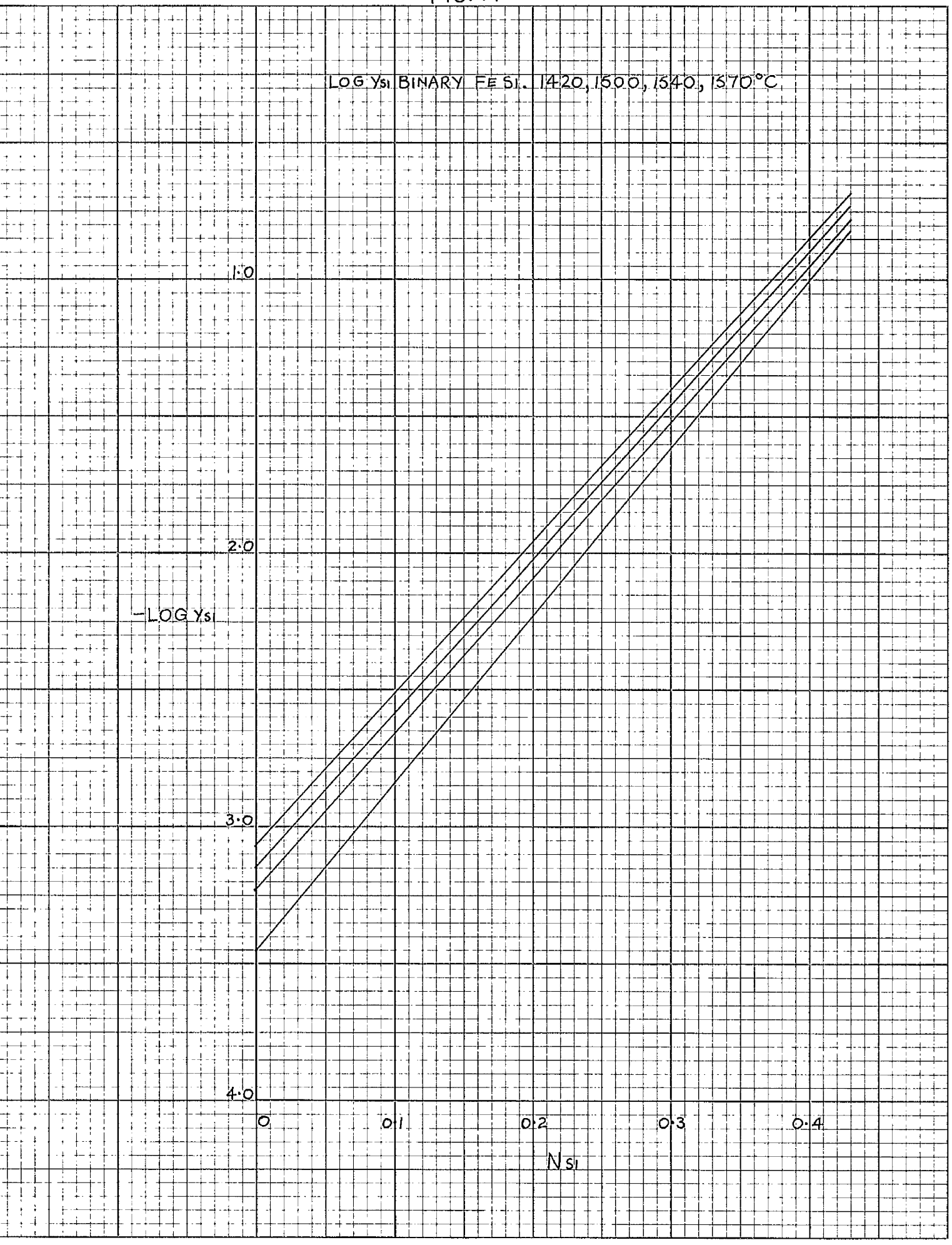
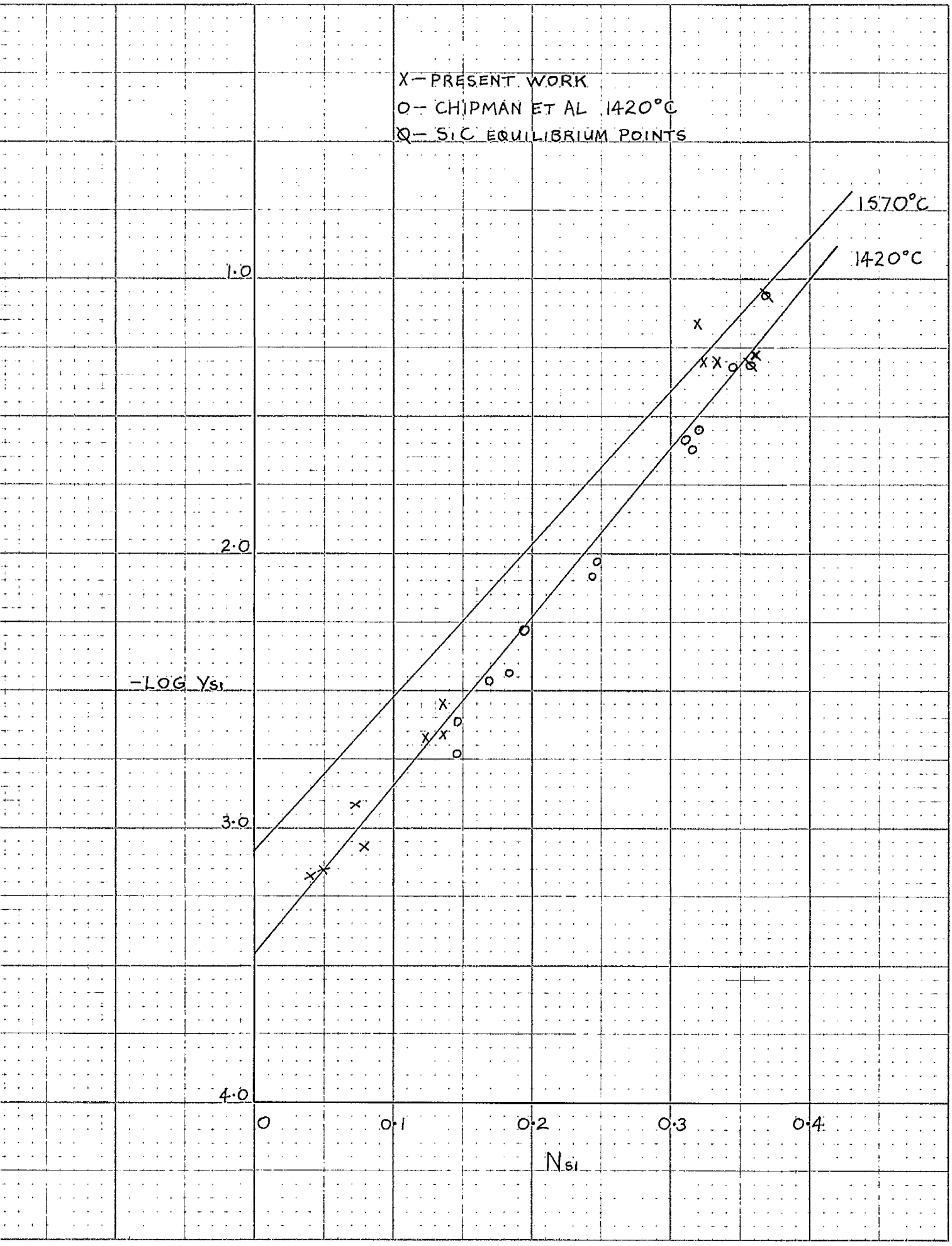

LOG Ysi BINARY FE SI. 1420, 1500, 1540, 1570°C
1·0
2·0
3·0
4·0
-LOG Ysi
0
0·1
0·2
0·3
0·4
Nsi

FIG. V


X — PRESENT WORK
O — CHIPMAN ET AL 1420°C
Q — SiC EQUILIBRIUM POINTS
1570°C
1420°C
1·0
2·0
3·0
4·0
-LOG Ysi
0
0·1
0·2
0·3
0·4
Nsi

their points would extrapolate to a value of $\log \gamma^{\circ}_{Si} = -3.50$ a difference of only 0.05 in $\log \gamma$, equivalent to an energy difference of about 400 cals.

Chipman et al[12] used an experimental arrangement to study the distribution of silicon between iron and silver, which differs in certain respects from that used in this work. They employed high frequency induction heating and held thecharge at temperature for 40 minutes in a silica crucible of 10 mm inside diameter. Temperatures were read on an optical pyrometer and controll ed by hand adjustment of the power input. Their heats were quenched by shutting off the power and passing a large volume of hydrogen through the furnace. The phases were then separated, ground clean, and analysed. Flowing argon was used to provide a n inert atmosphere during the runs. It is also probable that they employed a different method for analysing their silver samples.

In the present work, an electronically controlled, resistance furnace was used to heat a larger charge, in a 1 inch diameter silica crucible under a stagnant argon atmosphere, for at least 5 hours, and samples were extracted from the liquid melt. The procedure is detailed in the experimental section. The cumulative effect of these variations in experimental technique is probably reflected in the small difference appearing between the two sets of results as seen in the curve of Fig. V. The

remaining, possible, contributing factor is that of the temperature correction applied in adjusting the results to a common temperature. This involves a third source of data, viz. that of Korber and Oelsen[19] on the heat of mixing of liquid silicon and iron. They obtained the heat of mixing of the liquids at 1600°C by a calorimetric method, and their results were later confirmed by Chipman and Grant[33] using an entirely different technique. Since the temperature dependence of the heat of mixing is not known, the partial molal enthalpy of silicon, L_{Si}, is taken only as a function of composition. Values of L_{Si} corresponding to each mole fraction, N_{Si} are taken from Fig. III, and used in the expression $\frac{d \ln \gamma_{Si}}{d T} = \frac{-L_{Si}}{RT^2}$ to obtain the temperature correction.

Between the temperature 1420°C at which Chipman et al obtained their results, and 1570°C of the present work, the temperature correction reduces to $\pm L_{Si} \times (0.0105)$ where L_{Si} is in Kilocaloric units. It is clear that to make a significant error in the temperature correction, a very large error in L_{Si} is needed. Since good agreement has been obtained by two different sources[19,33] on the heat of mixing of silicon and iron at 1600°C it is most unlikely that a significant error is present in L_{Si}. The temperature adjustment can therefore be discounted as a source of error affecting the values of $\log \gamma_{Si}$.

Independent checks on the values of $\log \gamma_{Si}$ at fixed points can be obtained from equilibrium data as outlined by Chipman et al[11]. In view of the correction[24,25,26] applied to the heat of formation of silica, the original calculations of Chipman et al[11] now become obsolete. The same equations, however, can be used in the light of the more recent data to check the curve of $\log \gamma_{Si}$ vs N_{Si} obtained from the present work.

Activity of Silicon from Equilibrium Data

Silicon Carbide Equilibrium

Chipman et al[11] have measured the concentrations of silicon and carbon in liquid iron in equilibrium with silicon carbide over a range of temperatures. From their results, given as two linear curves of N_{Si} and N_C plotted against temperature, the following data are obtained.

At 1570°C, in the ternary Fe-Si-C solution in equilibrium with SiC and graphite $N_{Si} = 0.366$ and $N_C = 0.0144$. From equation (4) the activity of silicon

$$Si_{(L)} + C_{(gr)} = SiC \quad , \quad \Delta G^\circ_T = -28,000 + 8.74T \qquad (4)$$

in this solution is $a_{Si} = 0.0385$. Hence the activity coefficient of silicon, $\gamma^T_{Si} = 0.1053$, in the ternary solution. The effect of carbon on the activity coefficient of silicon in these solutions is expressed by the following equation

$$\log \gamma^{c}_{Si} = 6{\cdot}0\, N_c$$

where γ^{c}_{Si} is defined as $\gamma^{c}_{Si} = \gamma^{T}_{Si} / \gamma_{Si}$ (γ_{Si} referring to the binary Fe-Si solutions). The factor 6·0 in this equation is taken from the results of the present work on the Fe-Si-C solutions and will be discussed later. Since N_c = 0·0144, then from the above equations, γ^{c}_{Si} = 1·22 and log γ_{Si} = -1·06 in the corresponding binary solution. The value of log γ_{Si} obtained from the distribution study at 1570°C at N_{Si} = 0·366, is log γ_{Si} = -1·05. Furthermore, at 1420°C, Chipman et al[11] report that a solution containing N_c = 0·0105 and N_{Si} = 0·355 is in equilibrium with graphite and silicon carbide. For the corresponding Fe-Si binary solution these data give log γ_{Si} = -1·31. When the distribution study curve of the present work at 1570°C, is adjusted to 1420°C, it gives a value of log γ_{Si} = -1·27 at N_{Si} = 0·355.

The curves at 1570°C and 1420°C of log γ_{Si} vs. N_{Si} obtained from the present work are shown in Fig. V and the points calculated from the silicon carbide equilibrium data are marked for comparison. The agreement is good and provides confirmation of the validity of the several sets of experimental data used in calculating values of log γ_{Si}.

Activity of Silicon from Fe-Si-O Equilibria

The activity of silicon in binary liquid Fe-Si solutions can also be obtained from the data pertaining to the equilibria which may be established when solutions of silicon and oxygen in liquid iron are equilibrated with gas mixtures of hydrogen and water. The liquid melt is held in a silica crucible and at equilibrium the reactions taking place are described by the following equations.

$$SiO_2(s) + 2H_2(g) = \underline{Si} + 2H_2O \quad .....(7)$$

$$H_2O(g) = H_2(g) + \underline{O} \quad .....(8)$$

$$SiO_2 = \underline{Si} + 2\underline{O} \quad .....(6)$$

These equilibria have been extensively investigated by Gokcen and Chipman[11], then Matoba, Gunji and Kuwana[15] and later Chipman and Pilley[16] who summarised the results of all three sets of experimental data. These investigations all followed a similar experimental approach to the problem.

The gas mixture was made up by passing hydrogen through a constant temperature, saturating vessel containing pure water or lithium chloride solution. This mixture was then diluted approximately by four times with argon gas, in order to prevent a concentration gradient arising in the furnace tube through thermal diffusion in the gas phase. This controlled, gaseous mixture was passed over the liquid iron-silicon alloy contained in a silica crucible held at temperature in an induction heated

furnace. Samples were taken during runs by suction into silica tubes, and temperatures measured on calibrated optical pyrometers. A feature of these experiments was the length of time elapsing before equilibrium was judged to have been established. Chipman and Pillay[20] report runs continued at least 6 hours and in some cases 12 hours. Matoba, Gunji and Kuwana[16] report that 10 to 20 hours were required.

Since the liquid melt is saturated with silica, the relationship between the gas composition and the silicon concentration of the solution is expressed by a plot of $\log K'_7$, against % Si where K'_7 is given by

$$K'_7 = [\%Si] \left(\frac{p_{H_2O}}{p_{H_2}}\right)$$

This curve is linear over the concentration range studied, 0 - 3% Si in metal, and extrapolation to zero silicon will give the equilibrium constant

$$K_7 = a_{Si} \left(\frac{p_{H_2O}}{p_{H_2}}\right)^2$$

with the infinitely dilute solution as reference state.

The activity coefficient of silicon, f_{Si}, is given by the product $f_{Si} = f^{Si}_{Si} \cdot f^{o}_{Si}$ where the interaction coefficients f^{Si}_{Si} and f^{o}_{Si} express the effect of silicon and oxygen respectively, on the activity coefficient of silicon. Hence

$$K_7 = [\%Si] \cdot f_{Si} \cdot \left(\frac{p_{H_2O}}{p_{H_2}}\right)^2 = K'_7 \cdot f_{Si} = K'_7 f^{Si}_{Si} \cdot f^{o}_{Si}$$

$$\text{or } \log f_{Si} = \log f^{Si}_{Si} + \log f^{o}_{Si} = \log K_7 - \log K'_7$$

at the low concentrations of oxygen present in these solutions, its influence on f_{Si} is considered negligible so that f^{o}_{Si} 1 and

$$\log f_{Si} = \log f^{Si}_{Si} = \log K_{7} - \log K'_{7}$$

Using these equations a curve of $\log f^{Si}_{Si}$ was drawn against %Si at temperatures 1570°C, 1625°C and 1660°C from the results of Matoba, Gunji and Kuwana[15]. Their data agree with the results of Pilley and Chipman[16] and with those of Gokcen-Chipman[14] below 1% silicon. The earlier results of Gokcen and Chipman[14] above 1% silicon are now thought to have failed to come to equilibrium.

The curves obtained by Matoba, Gunji and Kuwana[15] are shown in Fig. VI and also that obtained at 1600°C by combination of the results of Pilley and Chipman[16], Gokcen and Chipman[14].

The slope of each line gives the value of e^{Si}_{Si}, defined as $d \log f_{Si}/d[\%Si]$. The temperature dependence of the equilibrium in (5) is given by the following equations:-

$$\log K_{7} = -15,640/T + 4{\cdot}65 \; , \; \Delta G^{o}_{5} = 71,540 - 22{\cdot}17\,T$$

$$e^{Si}_{Si} = 3,910/T - 1{\cdot}77$$

The results of a study of reaction (8) by Floridis and Chipman[23] led to the following equation

$$H_2O_{(g)} = H_{2(g)} + \underline{O} \quad \Delta G^{o}_{T} = -32,200 + 14{\cdot}63T \qquad (8)$$

Combining this free energy change with that for reaction (7) from Matoba et als' results, gives for reaction (6)

$$SiO_{2(s)} = \underline{Si} + 2\underline{O} \quad \Delta G^{o}_{T} + 135,940 - 51{\cdot}43T \qquad (6)$$

This reaction equation can now be combined with the revised free energy equation for silica[24] and with that for the free energy of solution of oxygen in liquid iron[11] to give the free energy equation for the solution of liquid silicon in iron (reaction 11)

$$Si_{(L)} + O_{2(g)} = SiO_{2(quartz)} \qquad \Delta G^{\circ}_{T} = -226,260 + 47{\cdot}34\ T \qquad (9)$$

$$O_{2(g)} = 2\,\underline{O} \qquad \Delta G^{\circ}_{T} = -56,440 - 1{\cdot}14\ T \qquad (10)$$

$$Si_{(L)} = \underline{Si} \qquad \Delta G^{\circ}_{T} = -33,880 - 2{\cdot}95\ T \qquad (11)$$

From equation (11) at 1570°C the free energy change is -39,310 cals.

Hence $-39,310 = 4{\cdot}575 \times 1643 \log a_{Si(dil.\ soln)}/(a_{Si(pure\ liquid\ Si)}$

Hence $a_{Si(dil.soln)}/a_{Si(\ )} = 0{\cdot}0000219$

In dilute solution, $N_{Si} = 0{\cdot}0199$ (%Si) $\therefore \gamma^{\circ}_{Si} = \frac{0{\cdot}0000219}{0{\cdot}0199}$

and $\log \gamma^{\circ}_{Si} = -2{\cdot}96$.

The extrapolated value of $\log \gamma_{Si}$ obtained from the present study at 1570°C is -3·08. The gradient of the two curves of activity coefficient against concentration can also be compared through Matoba et al's[15] equation

$$d \log f_{Si}/d[\%Si] = \epsilon^{Si}_{Si} = 3,910/T - 1{\cdot}77$$

This equation at 1570°C leads to a value of $\epsilon^{Si}_{Si} = d \ln \gamma_{Si}/d N_{Si}$ of $\epsilon^{Si}_{Si} = 29{\cdot}4$. The gradient ϵ^{Si}_{Si} obtained through the present distribution study is 13·6. The two curves at 1570°C are shown for comparison in Fig. VII. The discrepancy between the two sets of results is obviously beyond the limits of experimental error and indicates that in one of them, the desired

FIG. VI

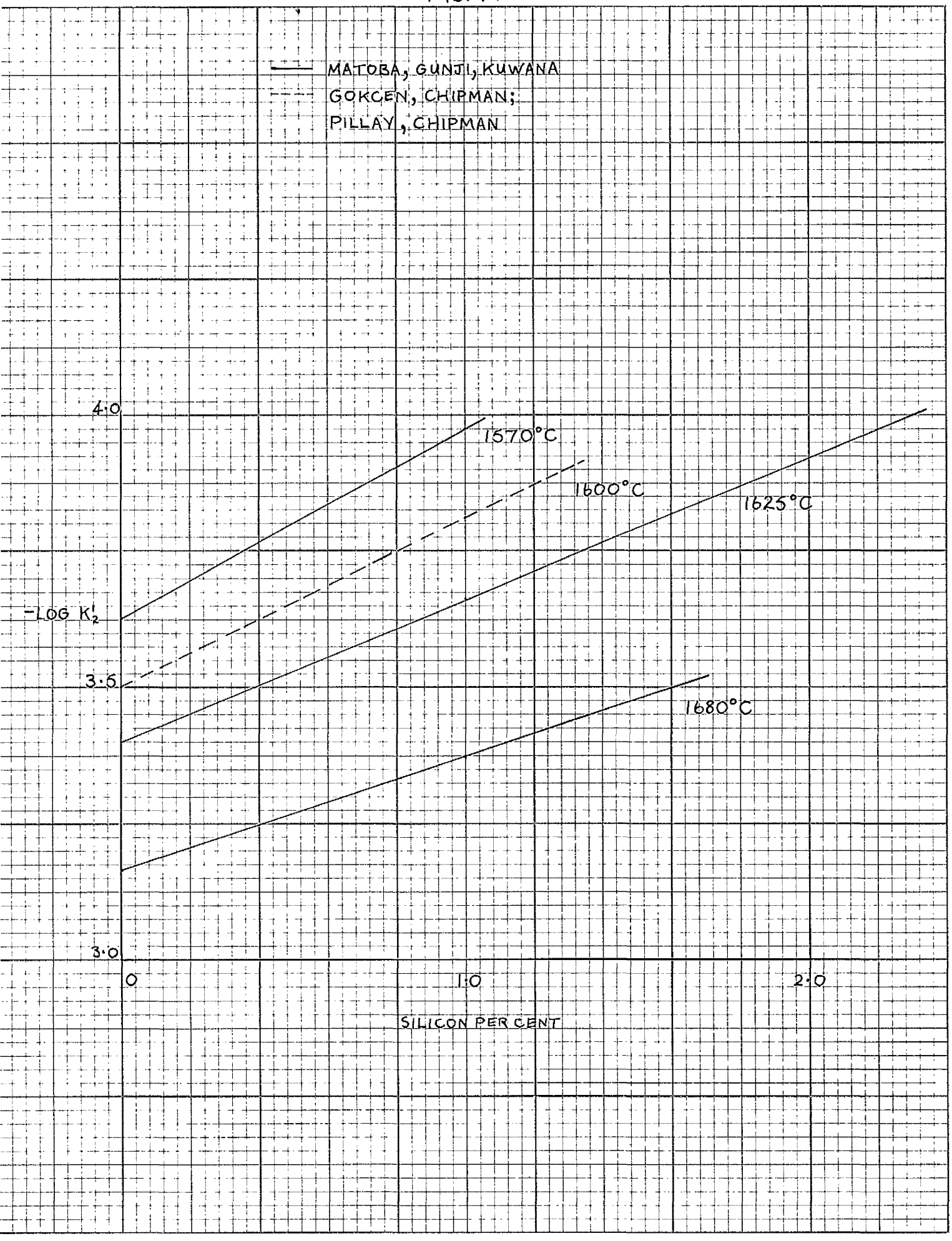
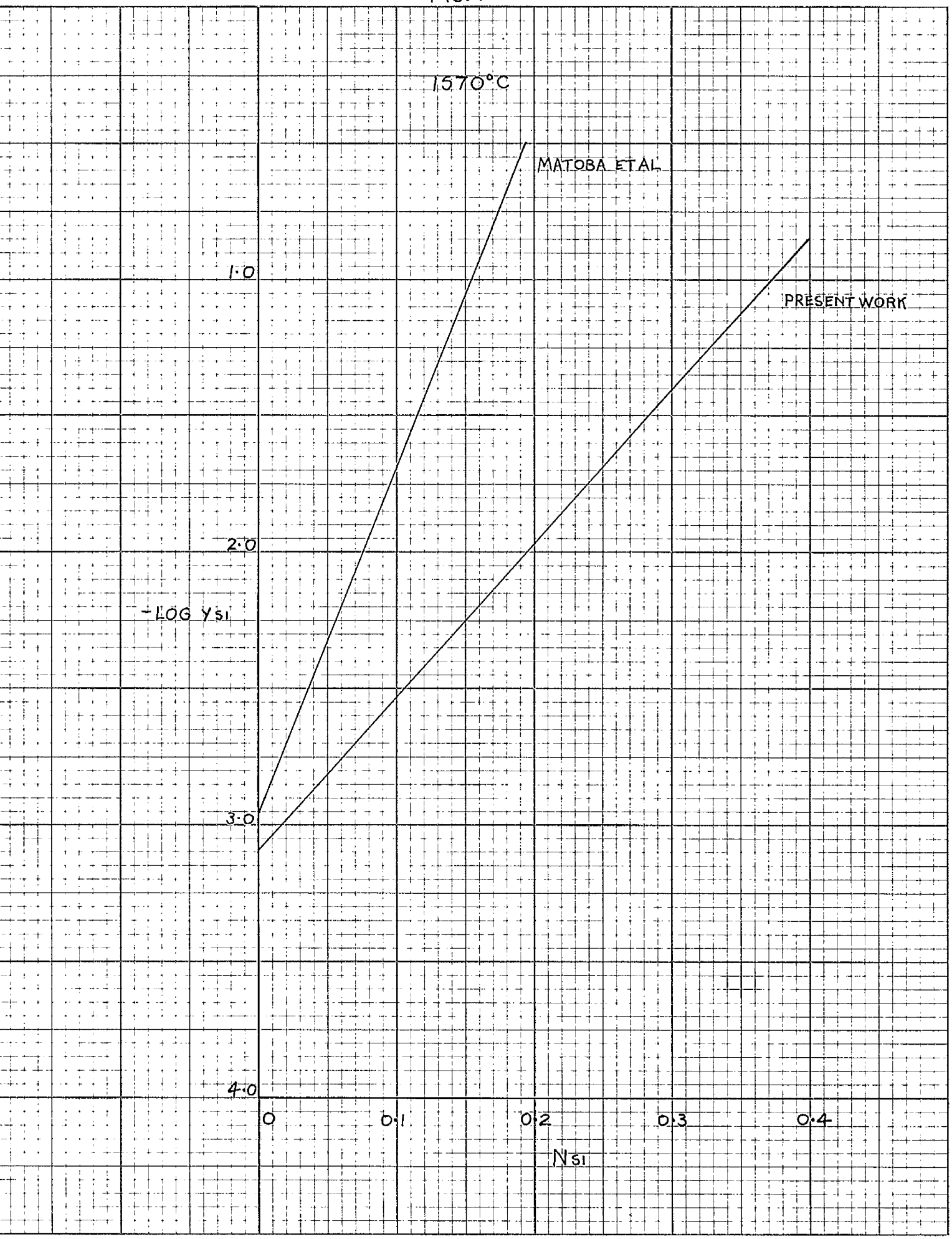

MATOBA, GUNJI, KUWANA
GOKCEN, CHIPMAN;
PILLAY, CHIPMAN
4·0
1570°C
1600°C
1625°C
-LOG K'2
3·5
1680°C
3·0
0
1·0
2·0
SILICON PER CENT

FIG. VII


1570°C
MATOBA ETAL
PRESENT WORK
1·0
2·0
3·0
4·0
-LOG Ysi
0
0·1
0·2
0·3
0·4
Nsi

equilibria have not been attained. A possible explanation of the anomaly has been suggested by Bell[34] as follows.

In the experimental arrangement of the work of Gokcen and Chipman[14], Pillay and Chipman[15], Matoba et al[16], a mixture of water and hydrogen was passed over the metal alloy contained in a silica crucible. Under these conditions the following reaction will take place.

$$SiO_2 + H_2 = SiO + H_2O \quad \ldots\ldots (13)$$

The concentration of silicon in the melt will be constant and governed by the silica dissociation (reaction 6).

$$SiO_2 = \underline{Si} + \underline{2O} \quad \ldots\ldots (6)$$

The value of p_{H_2O} however will be increased at the surface of the melt through reaction (13) so that the true p_{H_2O} pressure will be greater than the measured inlet pressure. In reaction (13)

$$K_{13} = p_{SiO} \cdot p_{H_2O}/p_{H_2}$$

If it is assumed that reaction (13) comes to equilibrium, for each molecule of SiO formed one molecule of H_2O is produced. If 'a' represents inlet p_{H_2O}, then $K_{13} = p.(a + p)/p_{H_2}$ where $p = p_{SiO} = p_{H_2O}$ from (13).

From these equations it can be seen that p_{H_2O} from reaction (13) will increase as the inlet water pressure decreases,

i.e. as the silicon concentrations increase in the melt.

The curve of $\log \gamma_{Si}$ vs N_{Si} calculated from the inlet pressure of p_{H_2O} through reaction (7).

$$SiO_{2(s)} + 2H_2O_{(g)} = \underline{Si} + 2H_2O \quad \ldots\ldots \quad (7)$$

will thus increasingly diverge from the true curve as N_{Si} increases. As can be seen from Fig. VII the two curves do in fact diverge in this manner. Ramstad and Richardson[22] have recently studied reaction (13) and obtained the following equation.

$$H_2 + SiO_2 = SiO + H_2O \quad \Delta G^\circ_{1700 - 1900\,^\circ K} = 127{,}000 - 45{\cdot}0T \quad (13)$$

Values of K_{13} at 1625° and 1570°C from this equation were used to calculate from Matoba et al's[15] inlet water pressures the probable p_{H_2O} values at the melt surfaces. These calculations involved the assumptions that (A) reaction (13) came to equilibrium, (B) that Matoba et al[15] used a 4·1 argon gas ratio. The latter was not reported.

The corrected water pressures were then used to recalculate $K'_7 = [\%Si](p_{H_2O}/p_{H_2})^2$ from Matoba et al's[15] data.

The derived values of K'_7 were found to be constant and at 1625°C $\log K'_7 = -3{\cdot}45$, at 1570°C $\log K'_7 = -3{\cdot}73$.

In view of the assumptions made in calculating these results, their significance lies in demonstrating the magnitude of the error which can arise through neglecting reactions involving the volatile species SiO. There is also strong evidence which

indicates that a reaction involving SiO did occur.

Chipman and Pilley[16] reported that in their work "attempts to extend the study to higher silicon concentrations were unsuccessful on account of the transfer of silica from the metal bath to the upper portions of the crucible by means of a silicon monoxide mechanism." This remark also suggests another reaction is possibly involved here between the silicon in the melt and its gaseous atmosphere:-

$$\underline{Si} + H_2O_{(g)} = SiO_{(g)} + H_{2(g)} \quad \ldots\ldots \quad (16)$$

This reaction would oppose reaction (13) in removing steam from the melt surface and it is fairly certain that the correction in p_{H_2O} calculated from reaction (13) is too high.

The word of Ramstad and Richardson[22] on reaction (13) however shows that this reaction will have to be considered

$$SiO_2 + H_2 = SiO + H_2O \quad \ldots\ldots (13)$$

before true values of p_{H_2O} are known with certainty. These workers used a carrier gas entrainment technique to measure p_{SiO} in reaction (13) by passing a $H_2 - H_2O$ mixture through solid silica at 1560°C and weighing the reformed silica in a condenser tube. Their results indicate that the reaction proceeds according to equation (13). They also studied the following reaction (14) using argon as carrier gas.

$$SiO_2 + Si \quad 2SiO \quad \Delta G^\circ_{1685 - 1800\,^\circ K} = 151{,}300 - 70{\cdot}07\,T \quad ..(14)$$

Ramstad and Richardson[22] also attempted to obtain values for the activity of silicon in iron through reaction (16). To do this

they suspended an iron bead in an atmosphere

$$\underline{Si} + H_2O_{(g)} = SiO_{(g)} + H_{2(g)} \qquad \ldots\ldots(16)$$

of H_2, H_2O and SiO obtained by passing hydrogen gas through silica at 1560°C. This bead at equilibrium had picked up 10% Si, i.e. 0·16 mole fraction. An equilibrium constant for reaction (16) was calculated from the free energy data on reactions (13) and (14) giving -

$$K_{16} = a_{Si} \times p_{H_2O}/p_{SiO} \times p_{H_2} = 2{\cdot}63 \times 10^{-3} \text{ at } 1560°C$$

Since $p_{SiO} = p_{H_2O}$ and $p_{H_2} = 1$ atmosphere then $K_{16} = a_{Si}$. From this, they calculated $\log \gamma_{Si} = -1{\cdot}835$ at $N_{Si} = 0{\cdot}16$, at 1560°C. Compared with the value obtained from the present work at 1570°C, this differs by 0·27 in $\log \gamma_{Si}$, equivalent to an energy difference of 2·5 kilocalories. Ramstad and Richardson[33] state that from a consideration of entropy data there appears to be a hidden consistent error running through their results. It would seem that this error is mainly associated with reaction (13) and that a correction of approximately 2 kilocalories would bring their data into good agreement with that of both Schafer and Hornle[35], and the present work.

In view of these considerations, it would also appear that the activity coefficients of silicon in iron calculated from the data of Gokcen and Chipman[14], Matoba et al[15], and Pillay and Chipman[16], cannot be considered reliable until they have been corrected for the effects of side reactions involving silicon monoxide. When

the free energy data used to calculate the equilibrium in reaction (16) is placed on a sure basis, the method of Ramstad and Richardson[23] will provide another means of checking activity values of silicon obtained from the distribution experiments. A better

$$Si + H_2O_{(g)} = H_{2(g)} + SiO_{(g)} \quad \ldots\ldots\ldots(16)$$

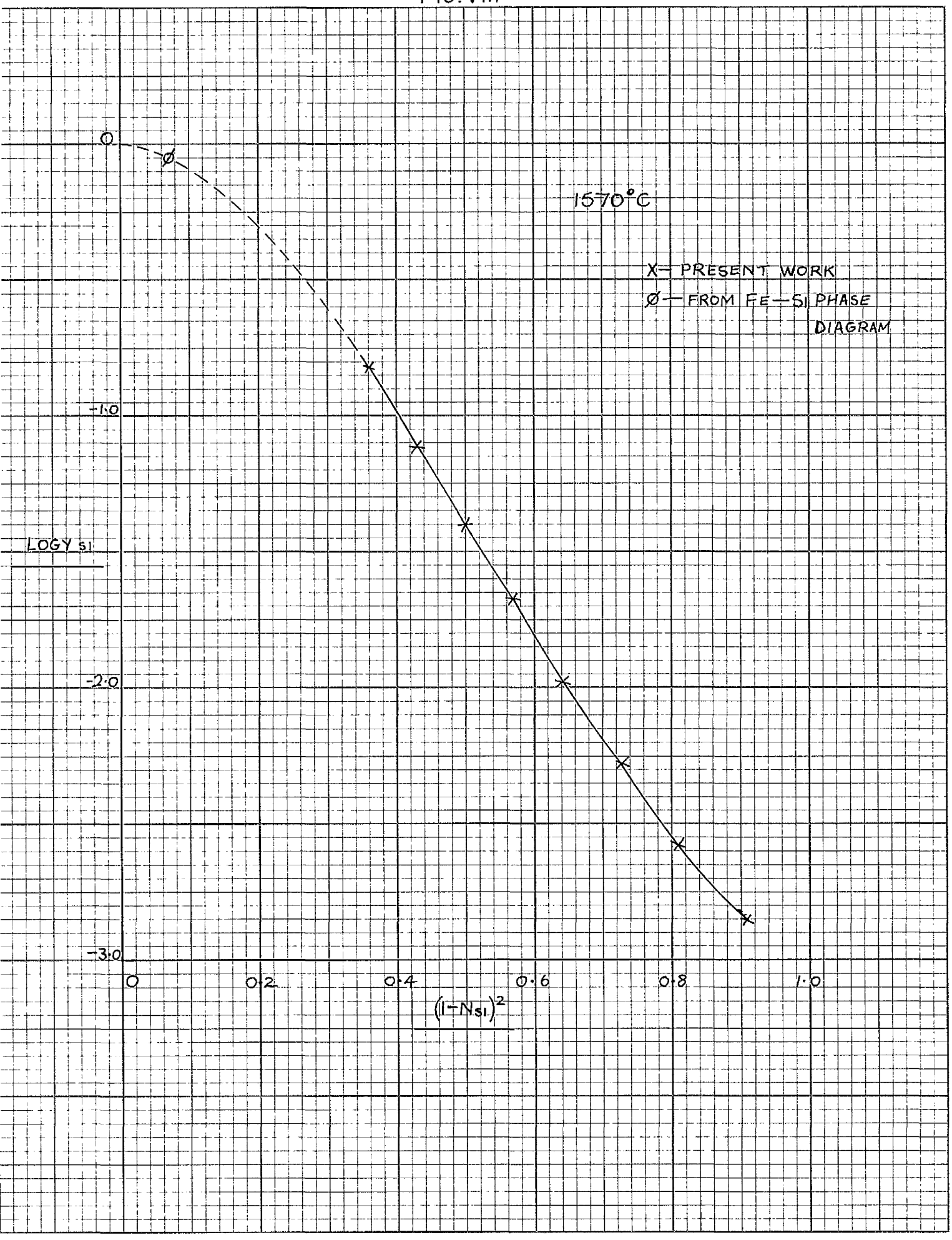
interpretation might also be made then of the experiments[14,15,16] on the silicon-oxygen equilibria in liquid iron.

Activity of Silicon from the Fe-Si Phase Diagram

Chipman et al[11] in their earlier work on the distribution experiments of silicon between iron and silver, used a point of known silicon activity to convert their distribution curve of $\log N_{Si}^{Ag}/N_{Si}^{Fe}$ to one of $\log \gamma_{Si}$. Unfortunately this conversion was based on an extrapolation which assumed a constant value of the function $\log \gamma_{Si}/(1-N_{Si})^2$. This assumption is not valid and led to an incorrect calibration of the activity coefficient curve. The value of the activity coefficient at this fixed point however is still valid and its derivation as given by Chipman et al[11] is as follows. At 1207°C pure solid silicon is in equilibrium with a solution in which $N_{Si} = 0.73$. The melting point of silicon is 1414°C and its heat of fusion 11,100 cals/gr atom. Hence at 1207°C $\gamma_{Si} = 0.84$. From the data of Korber and Oelsen[10] shown in Fig. III, L_{Si} in this solution is -1.2 K cals. From the relationship

$$d \ln \gamma_{Si}/d T = - L_{Si}/RT^2$$

FIG. VIII

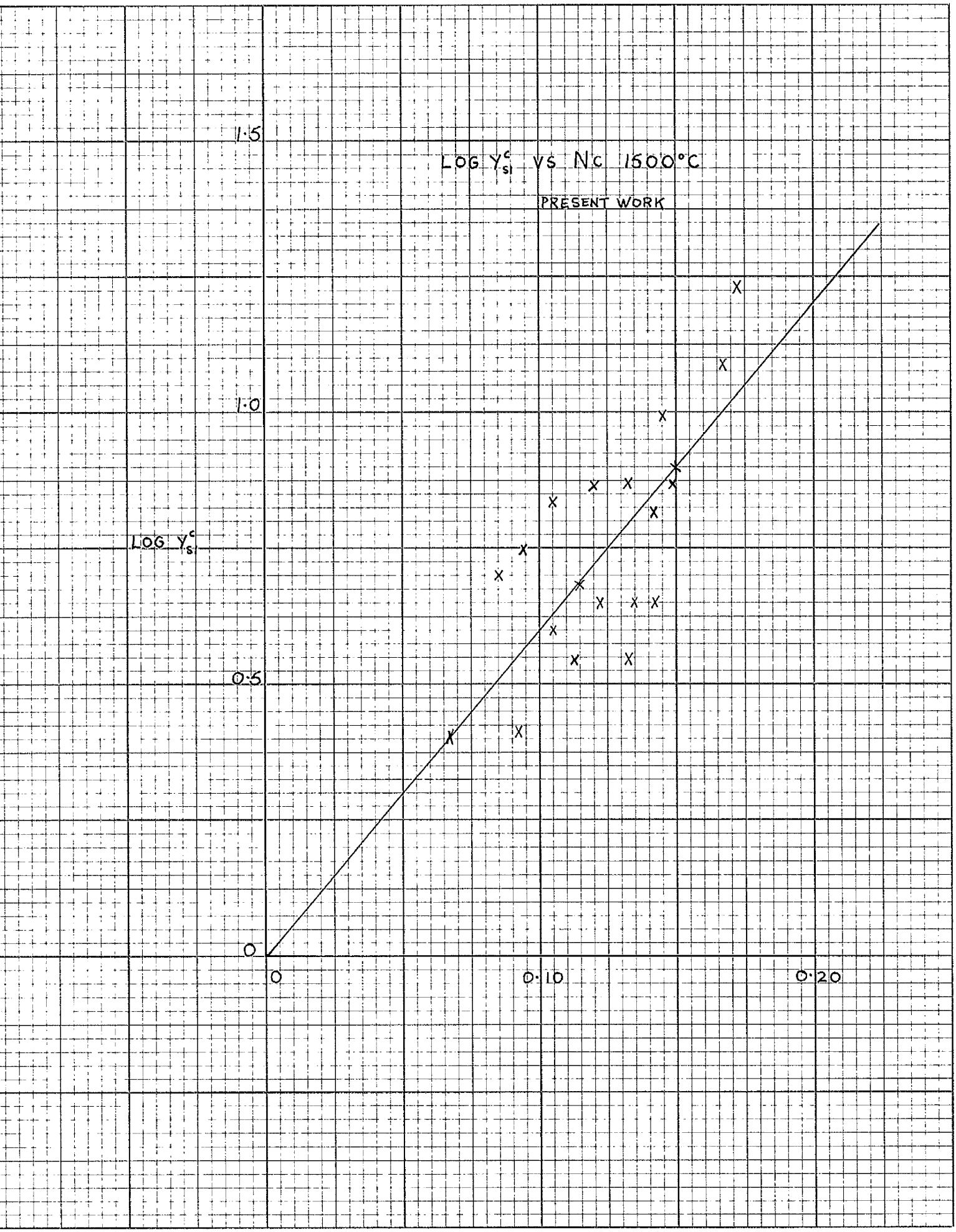

0
-1·0
-2·0
-3·0
LOGY Si
0
0·2
0·4
0·6
0·8
1·0
(1-N Si)²
1570°C
X— PRESENT WORK
Ø— FROM Fe—Si PHASE DIAGRAM

the effect of temperature is obtained by giving $\gamma_{Si} = 0.905$ at 1570°C, i.e. $\log \gamma_{Si} = -0.05$ at $N_{Si} = 0.73$. Values of $\log \gamma_{Si}$ at 1570°C, taken from the best straight line through the $\log \gamma_{Si}$ curve of the present work have been used to construct the curve of $\log \gamma_{Si}$ vs $(1 - N_{Si})^2$ shown in Fig. VIII and included is the point calculated above from the Fe-Si phase diagram data. It is clear from the shape of the curve that this point alone could not be used with certainty to fix the scale of the $\log \gamma_{Si}$ curve. Used in the content of Fig VIII, however, it provides added confidence in the validity of the activity coefficient curve obtained from the present work.

Activity of Silicon in Liquid Fe-C-Si Solutions

To obtain values for the activity of silica in lime-silica and lime-alumina-silica slags, Fulton and Chipman,[4] then Langenburg and Chipman[9] based their calculations on a knowledge of the activity of silicon in carbon saturated iron, obtained from their earlier distribution studies[11]. In the ternary Fe-Si-C solutions the results of Chipman et al[11] did not extend beyond $N_C = 0.08$. The aim of the present work was to increase this range, having established in the binary Fe-Si solutions reliable activity values of silicon at the lowest N_{Si} concentrations, corresponding to the higher carbon concentrations in the ternary solutions.

FIG. IX



Experiments were therefore carried out on the distribution of silicon between liquid silver and liquid iron-carbon-silicon solutions. The same method was employed as for the binary Fe-Si solutions and the results are given in Table II. These are plotted in Fig. IX as $\log \gamma^{c}_{Si}$ (defined in Chapter I) vs N_c. The range of carbon concentrations extends from $N_c = 0.07$ to 0.17. There is a fairly large scatter of the experimental points in this plot for which there is no obvious reason. A similar scatter exists in the results of both Chipman et al[11] and Ohtani[36] for this function - $\log \gamma^{c}_{Si}$ - nor is it clear from any of the data if the relationship is linear. Chipman et al[11] considered their results at 1420°C to be best expressed by the linear equation $\log \gamma^{c}_{Si} = 5.5N_c$. The best straight line drawn through the results of the present work would have the equation $\log \gamma^{c}_{Si} = 6.0\ N_c$ at 1500°C.

Ohtani[36] used an electrochemical method to study the activity of silicon in both the binary and ternary Fe-C-Si solutions. His experimental technique involved measurements of the E.M.F. values corresponding to a range of solutions of carbon and silicon incorporated in the following electrode concentration cell.#

* $Fe \cdot Si \cdot C \ / \ SiO_2, CaO, Al_2O_3, MgO \ / \ Si_{(L)}$ -

In this cell, pure liquid silicon is the standard reference electrode and a liquid slag containing silica forms the intermediate electrolyte. The two metals were melted in a two-legged magnesia

crucible, under argon or nitrogen, and the slag added to form an electrolyte bridge. Potentials across the cell were then measured by inserting 6 mm graphite and 2 mm molybdenum rods, connected to a potentiometer, into the liquid iron solutions and liquid silicon respectively. To prevent these leads dissolving, they were inserted only while a measurement was taken. Samples for analysis were withdrawn by a syringe after each reading. A platinum-platinum rhodium thermocouple was used to measure the temperature, 1540 ± 10°C.

The use of graphite and molybdenum rods as leads in the above measurements produces a thermal EMF between them which must be subtracted from the total EMF read to obtain the true potential difference of the cell. Ohtani measured this thermal EMF by inserting the leads into liquid silver and pig iron, at the same time measureing the liquid temperature with a Pt/Pt.Rh. thermocouple.

The following equation holds for the EMF of the cell, (E) and the activity of silicon at a given temperature T.

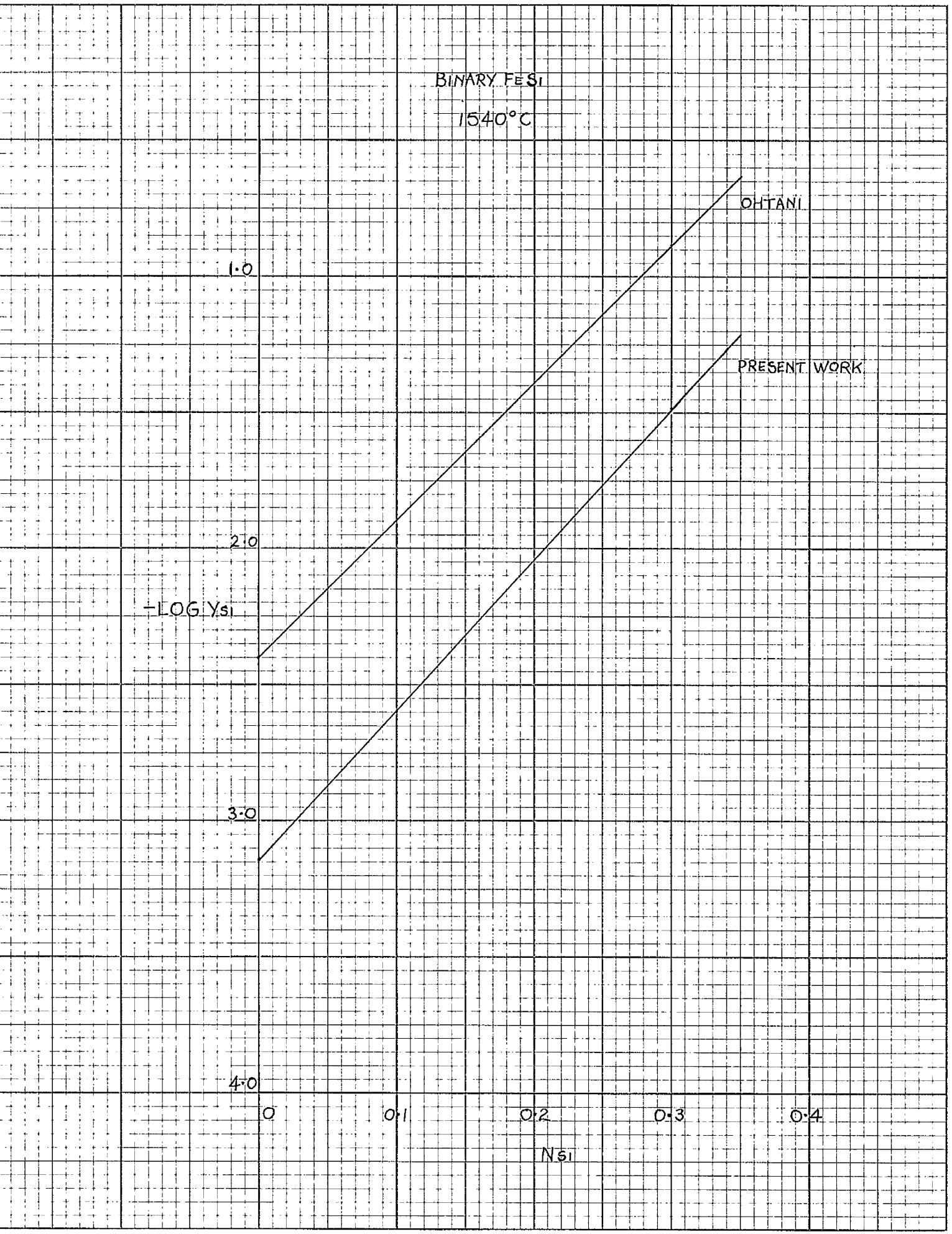
$$E = RT/n\ F\ \ln a'_{Si}/a_{Si} \qquad \text{.....(17)}$$

a'_{Si} and a_{Si} are the activities of the pure liquid silicon and the silicon in the liquid iron alloys respectively. With pure liquid silicon as the reference standard state, $a'_{Si} = 1$ and,

$$E = -(0.0002\ T/n) \log a_{Si} \qquad \text{.....(18)}$$

To obtain a value for n, the electron change in the cell reaction,

FIG. X


BINARY FeSi
1540°C
OHTANI
PRESENT WORK
1·0
2·0
3·0
4·0
−LOG YSi
0
0·1
0·2
0·3
0·4
NSi

Ohtani[36] assumed that silicon, dissolved in liquid iron, obeys Henry's Law and replaced a_{Si} by N_{Si} in (18). Substitution of corresponding values of E and N_{Si} gave values of n from 4·32 - 4·02, from which it was concluded that n = 4. Hence, putting n = 4 in equation (18) Ohtani[36] calculated silicon activities in the binary and ternary solutions, obtained values for γ_{Si} in both solutions, and derived the equation $\log \gamma^{o}_{Si} = 5{\cdot}3\ N_{C}$.

Although this equation is in close agreement with that of Chipman et al[11], activity values for the binary and ternary solutions taken from Ohtani's data[36] agree with neither Chipman et al[11] nor the results of the present work. There is a large consistent difference between Ohtani's[36] results and the results of Chipman et al[11] which is cancelled out in calculating values of $\log \gamma^{o}_{Si}$.

This difference is clearly brought out in Fig. 10 where the binary curve from Ohtani's[36] data is shown together with the curve from the present results both adjusted to 1500°C. Ohtani's curve of $\log \gamma^{o}_{Si}$ shows a large scatter which would confuse comparison and is not shown.

Regarding the difficult question of a cell reaction the following equation was suggested:-

$$n\ Si\ (in\ Fe) + 3\ n\ SiO_4^{4-}\ (slag) = 4\ n\ SiO_3^{2-}\ (slag) + 4\ e \quad \ldots (19)$$

The reduction in this manner of complex silicate ions close to the alloy electrode would certainly involve a four electron transfer as in (19). The equation however is speculative and cannot be

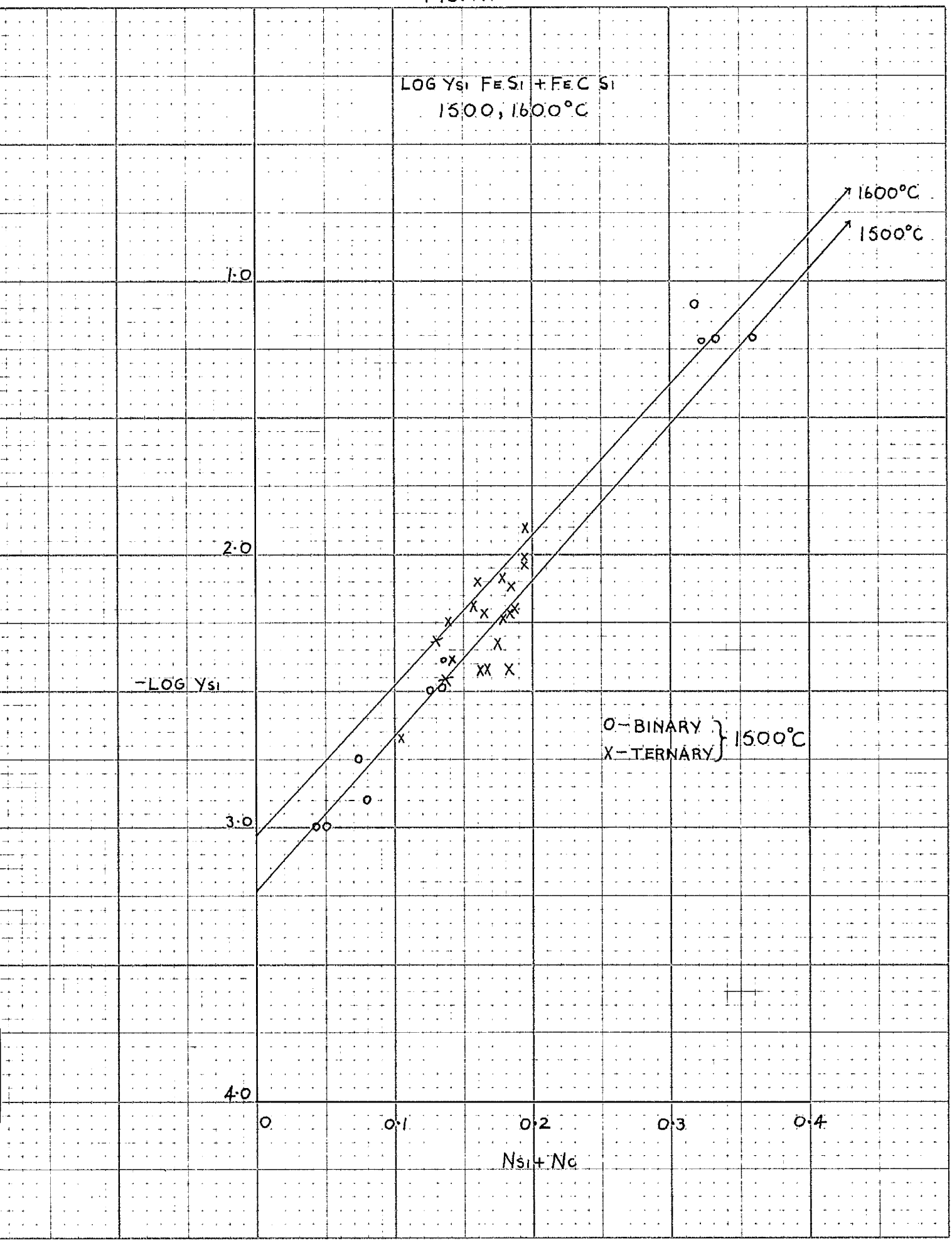
accepted as evidence that this reaction does involve 4 electrons. The assumption that Henry's Law is obeyed in liquid iron-silicon solutions is clearly incorrect and this invalidates Ohtani's method of calculating 'n', from his experimental data.

At 1500°C, values of the function $d \ln\gamma_{Si} / N_{Si}$ from the present work and Ohtani's[30] data are 14 and 11·7 respectively, showing some measure of agreement, but there is a difference of 0·76 in $\log \gamma^{\circ}_{Si}$. A similar difference appears between both sets of results on the ternary solutions. Before a proper interpretation of Ohtani's data can be made, the mechanism of the cell reaction and the electron transfer involved must be known with certainty. No reliance can therefore be placed on activity values calculated from Ohtani's data until all the terms in equation (16) are known.

The activity values of silicon in the binary and ternary solutions obtained from the present results can now be used in conjunction with the data of Chipman et al[3,4] to calculate silica activities in lime alumina-silica slags.

From the results of their distribution studies at 1420°C, Chipman et al showed that for the ternary Fe-C-Si solutions the curve of $\log \gamma_{Si}$ vs $(N_C + N_{Si})$ is essentially the same curve of $\log \gamma_{Si}$ vs N_{Si} for the binary solutions. This is substantially confirmed by the results of the present study at 1500°C shown in Fig. XI. The solubility of graphite as a function temperature and silicon content has been determined[11]. Temperature adjustment on the

FIG. XI


LOG Ysi FeSi + FeC Si
1500, 1600°C
1600°C
1500°C
1·0
2·0
3·0
4·0
-LOG Ysi
O-BINARY
X-TERNARY
1500°C
0
0·1
0·2
0·3
0·4
Nsi + Nc

$\log \gamma_{Si}$ vs N_{Si} curve can be made using the data of Korber and Oelsen[13]. Hence the activity of silicon in graphite saturated solution can be accurately determined.

Chipman et al[3,4] measured the equilibrium concentrations of silicon and silica in carbon saturated iron and slag solutions respectively, held at temperature under carbon monoxide gas at 1 atmosphere. The equilibrium is represented by the following reaction.

$$SiO_2(slag) + 2C_{(gr)} = \underline{Si} + 2CO\ (1atm)\ldots 2a$$

under these conditions $K_{2a} = \dfrac{a_{Si} \cdot P_{CO}^2}{a_{SiO_2} \cdot a^2 C} = \dfrac{a_{Si}}{a_{SiO_2}}$

K_{2a} can be obtained from the free energy equations for the formation of carbon monoxide[6] and silica (recently revised).

$$2C(s) + O_2(g) = 2\,CO_{(g)} \qquad \Delta G^\circ_T = -55{,}600 - 40{\cdot}80\ T$$

$$SiO_2(qu) = Si_{(L)} + O_2(g) \qquad \Delta G^\circ_T = 226{,}200 - 47{\cdot}34\ T$$

These two equations give for reaction 2a

$$\Delta G^\circ_T = 170{,}660 - 88{\cdot}14\ T = -RT \ln K_{1a}$$

At 1600°C, this equation gives $K_{2a} = 0{\cdot}231$, hence $a_{Si}/a_{SiO_2} = 0{\cdot}231$. In order to compare silica activities obtained by Kay and Taylor[2] with those recalculated here from the data of Chipman et al[3], eq uilibrium concentrations of silicon and silica have been taken from the ternary diagram of Chipman et al[3] at 1600°C, along a line

TABLE IV

$\%SiO_2$	%Si	N_{Si}	N_O	$-\log_{Si}$	$-\log a_{Si}$	a_{SiO_2}
20	4	•067	•163	1•76	2•82	•0072
24	8	•135	•118	1•66	2•49	•0155
29	12	•201	•079	1•52	2•24	•0275
32	16	•256	•048	1•37	1•92	•056
36	20	•325	•024	1•14	1•60	•120
40	22•4	•364	•010	0•97	1•40	•190

a_{SiO_2} recalculated from the data of Langenberg and Chipman[3].

FIG. XII

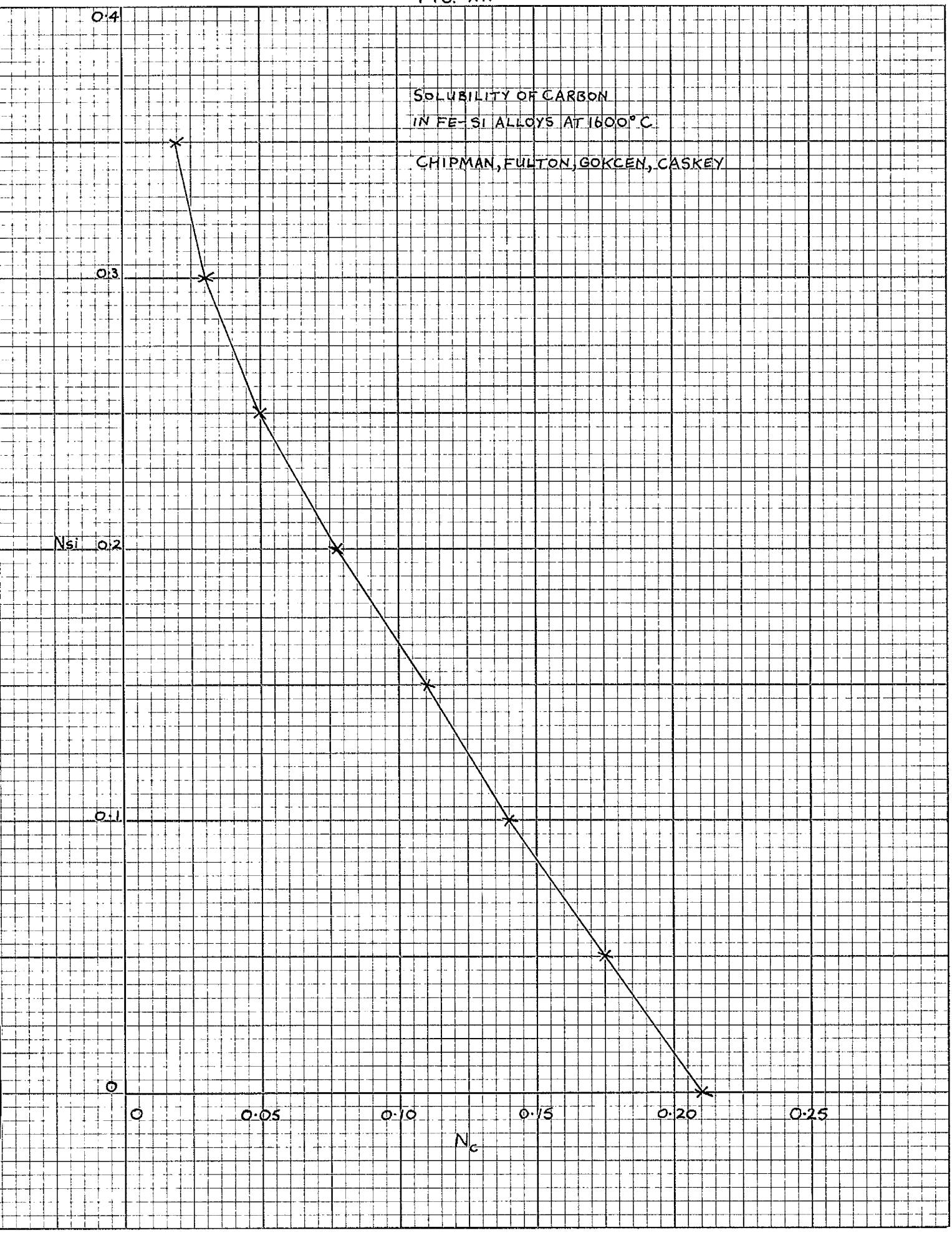
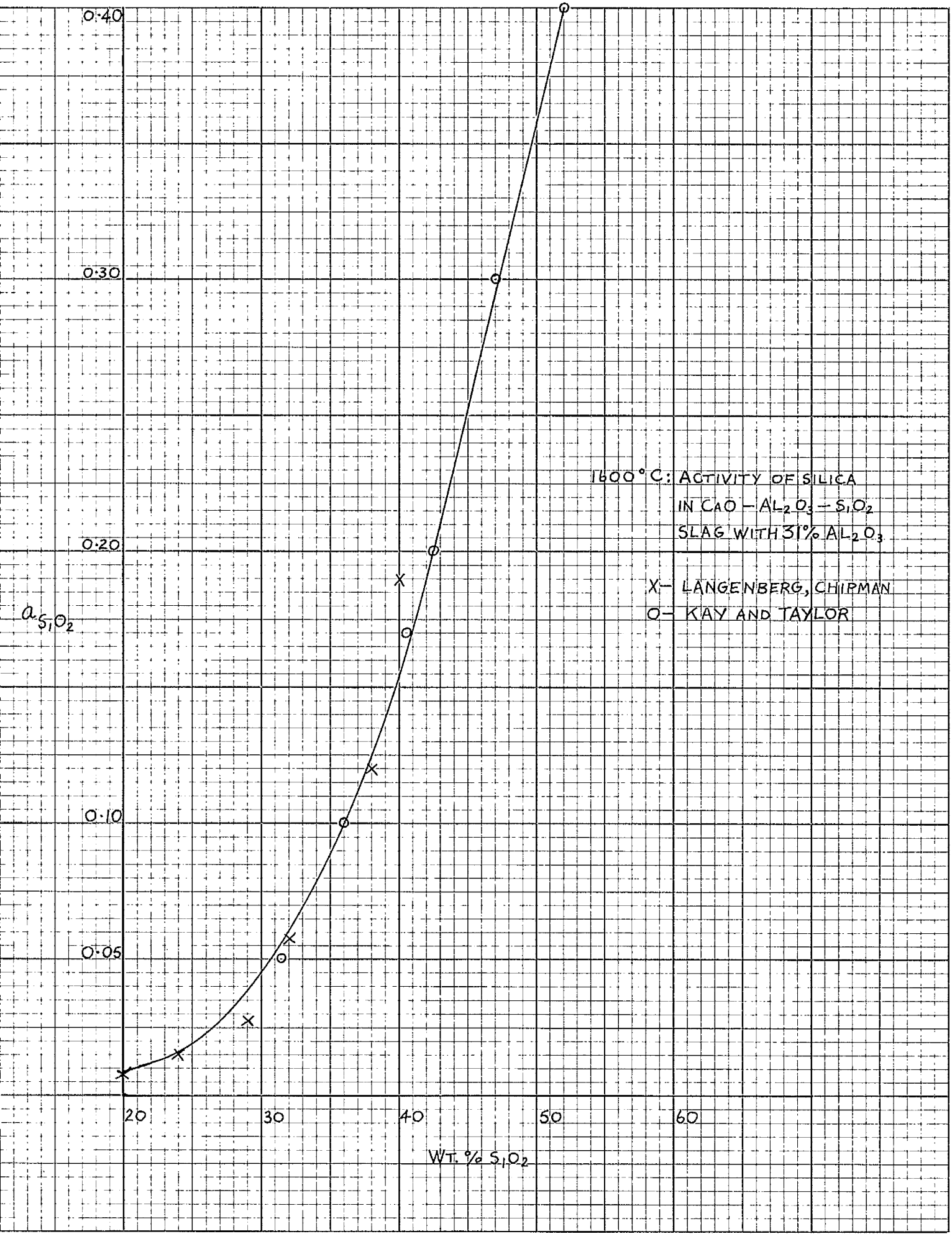

SOLUBILITY OF CARBON
IN FE-SI ALLOYS AT 1600° C.
CHIPMAN, FULTON, GOKCEN, CASKEY
0·4
0·3
Nsi 0·2
0·1
0
0
0·05
0·10
0·15
0·20
0·25
Nc

FIG. XIII


0·40
0·30
0·20
0·10
0·05
a_{SiO_2}
20
30
40
50
60
Wt. % SiO_2
1600° C: ACTIVITY OF SILICA IN $CaO - Al_2O_3 - SiO_2$ SLAG WITH 31% Al_2O_3
X– LANGENBERG, CHIPMAN
O– KAY AND TAYLOR

corresponding to 31% Al_2O_3 in the slag. Values of the concentrations of carbon in the liquid iron-silicon-carbon solutions are taken from the curve of Fig XII reproduced from the data of Chipman et al at 1600° C. Since the carbon solubility is greatly decreased by silicon the correction for its presence is small and has been neglected. Activity coefficients are read from the curve $(N_C * N_{Si})/\log \gamma_{Si}$ at 1600°C obtained from the present work and shown in Fig. XI. The resulting silicon activities and K_{2a} at 1600°C have been used to calculate values of a_{SiO_2} and these are collected in Table IV.

Values of a_{SiO_2} at 1600°C have also been taken from the ternary diagram of Kay and Taylor[2] along a line corresponding to 31% Al_2O_3. Both sets of data are shown in the curve a_{SiO_2} vs wt. % SiO_2 in Fig. XIII and are seen to be in good agreement.

The point at 23% silicon in Table IV corresponds to equilibrium with silicon carbide and the activity of silicon at this point has been calculated from the free energy equation for the formation of silicon carbide.

$$Si_{(L)} + C_{(gr)} = SiC \quad \Delta G^\circ_T = -28{,}000 + 8{\cdot}74\ T$$

The point is marked in Fig. XIII and is in good agreement with the data of both Kay and Taylor[2] and Chipman et al[3].

CHAPTER V

References

REFERENCES

1. D. Baird and J. Taylor, Trans. Faraday Soc., 1958, 54, 527.

2. D.A.R. Kay and J. Taylor, Trans. Faraday Soc., 1960, 56, 1372.

3. F.C. Langenberg, H. Kaplan and J. Chipman, The Physical Chemistry of Steel Making (J. Wiley and Sons, Inc.1958, Tech.Press) p. 65.

4. J.C. Fulton and J. Chipman, Trans. A.I.M.E., 1954, 200, 1136.

5. K. Sanbongi and Omori, Sci. Rep. Tohoku Univ. A., 1959, 11, 244.

6. J.P. Coughlin, U.S. Bur. Mines Bull., 542, 1954.

7. G.L. Humphrey, S.S. Todd, J.P. Coughlin and E.G. King, Bur. Mines Rept. Inv. 4888, 1952

8. Ibid.

9. J. Browart, G. De Maria, and M.G. Inghram, J. Chem. Phys., 29, 1015, 1958.

10. J. Chipman, Thermodynamic Properties of Blast Furnace Slags(Symp. Physical Chemistry of Process Metallurgy, Pittsburgh, 1959).

11. J. Chipman, J.C. Fulton, N.A. Gokcen and C.R. Caskey, Acta Met. 2 439, 1954.

12. Schadel, A.M. G. Darge and C.E. Birchenall, Trans.A.I.M.E., 188, 1950, 1017.

13. F. Korber and W. Oelsen, Mitt. Kaiser Wilhelm Inst. Eisenforch, 18, 109.

14. N.A. Gokcen and J. Chipman, Trans. A.I.M.E., 194, 171, 1952 and J. Metals, 1017, 1953.

15. S. Matoba, K. Gunji and T. Kuwana, Tetsu To Hagane 1959, 45, 229 Stahl u. Eisen, 1960, 80, 299.

16. J. Chipman and T.C.M. Pillay, Trans. Met. A.I.M.E., 221, 1961, 1277.

17. M.N. Bastur and J. Chipman, Trans. A.I.M.E., 185, 1949, 441.

18. L.S. Darken and R.W. Gurry, J.A.C.S., 68, 1947, 798.

19. J. Taylor and J. Chipman, Trans. A.I.M.E., 154, 1943, 228.

20. Nat. Bur. Standards 'Select Values of Chem. Thermodynamic Props.' 1948.

21. J. Chipman, J. Am. Chem. Soc., 83, 1762, 1951.

22. H.F. Ramstad and F.D. Richardson, Trans. Met. Soc. A.I.M.E., 221, 1021, 1961.

23. T.P. Floridis and J. Chipman, Trans. Met. Soc. A.I.M.E., 1958, 212, 549.

24. T. Cochrane and C. Foster, J. Chem. Phys, 66, 380, 1962.

25. W.D. Good, ibid, p.381.

26. S.S. Wise, J.L. Margrave, H.M. Feder and W.N. Hubbard, ibid

27. E.G. King, J. Am. Chem. Soc., 73, 656, 1951.

28. J.F. Elliot and R.D. Pehlke, Trans. Met. Soc. A.I.M.E., 215, 781, 1959.

29. Standard Methods of Analysis of Iron, Steel and Ferro-Alloys(United Steels Co's. Ltd)

30. A.I. Vogel, Textbook of Quant. Inorg. Analysis.

31. J. d'Entremont and J. Chipman, in press.

32. J. Hager, paper submitted to Trans. Met. Soc. A.I.M.E.

33. J. Chipman and N.J. Grant, Trans. Am. Soc. Metals, 31, 365, 1943.

34. H.B. Bell, private communication.

35. H. Schäfer and R. Hornle, Ztsch. Anorg. Allgem. Chemie, 1950, 263, 261.

36. M. Ohtani, Sci. Rep. R.I. Tohohu Univ. 7, 5, 1955, p.487.

A C K N O W L E D G E M E N T S

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